

**EXERCISE-1 (Subjective Questions)****RUTHERFORD'S MODEL OF ATOM**

- Q.1 An alpha particle having initial kinetic energy of  $6.4 \times 10^{-13}$  J is projected towards a silver foil in Rutherford's experiment setup. The atomic number of silver is 47. Calculate  
 (i) K.E. of the  $\alpha$ -particle at a distance of  $5 \times 10^{-14}$  m from the nucleus,  
 (ii) the shortest distance from the nucleus of silver to which the  $\alpha$ -particle reaches.
- Q.2 A beam of some kind of particle of velocity  $2 \times 10^7$  m/s is scattered by a gold ( $z = 79$ ) foil. Find specific charge of this particle (charge / mass) if the distance of closest approach is  $7.9 \times 10^{-14}$  m.
- Q.3 With what kinetic energy (eV) should an  $\alpha$ -particle travel towards the nucleus of a metal atom ( $Z=30$ ) so as to arrive at a distance  $10^{-14}$  meter from the nucleus of the metal atom ?
- Q.4 With what velocity should an  $\alpha$ -particle travel towards the nucleus of a Cu atom so as to arrive at a distance  $10^{-13}$  m.

**ELECTROMAGNETIC RADIATIONS & PLANCK'S QUANTUM THEORY**

- Q.5 Calculate the energy of a photon of sodium light of wave length  $5.862 \times 10^{-6}$  m in Joules.
- Q.6 Calculate the energy of 100 photons if the wavelength of the light is 2000 Å.
- Q.7 The eyes of certain member of the reptile family pass a single visual signal to the brain when the visual receptors are struck by photons of wavelength 132.6 nm. If a total energy of  $3 \times 10^{-14}$  J is required to trip the signal, what is the minimum number of photons that must strike the receptor.
- Q.8 Suppose  $10^{-17}$  J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ( $\lambda = 550$  nm) are needed to generate this minimum amount of energy. **28**
- Q.9 A certain dye absorbs 4700 Å and fluoresces at 5080 Å these being wavelengths of maximum absorption that under given conditions 47% of the absorbed energy is emitted. Calculate the ratio of the no. of quanta emitted to the number absorbed.
- Q.10 The quantum yield for decomposition of HI is 0.2. In an experiment 0.01 moles of HI are decomposed. Find the number of photons absorbed.
- [Given : Quantum yield =  $\frac{\text{number of molecules decomposed}}{\text{number of photons subjected}}$  ] **0.2 =  $\frac{0.01 \times 6 \times 10^{23}}{N}$**
- Q.11 Calculate the wavelength of the radiation that would cause photo dissociation of chlorine molecule if the Cl-Cl bond energy is 241 KJ/mol.  **$\frac{241 \times 10^3}{6 \times 10^{23}} = \frac{hc}{\lambda}$**
- Q.12 The dissociation energy of  $H_2$  is 430.53 KJ/mol. If  $H_2$  is exposed to radiant energy of wavelength 253.7 nm, what % of radiant energy will be converted into K.E.

- Q.13 Find the number of photons of radiation of frequency  $5 \times 10^{13} \text{ s}^{-1}$  that must be absorbed in order to melt one gm ice when the latent heat of fusion of ice is 331.5 J/g.
- Q.14 How many photons are emitted per second by a 5 mW laser operating at 620 nm?
- Q.15 A bulb emits light of  $\lambda = 4500 \text{ \AA}$ . The bulb is rated as 150 watt and 8 percent of the energy is emitted as light. How many photons are emitted by the bulb per second?

### PHOTOELECTRIC EFFECT

- Q.16 Calculate the binding energy per mole when threshold wavelength of photon is 240 nm.  
[Given :  $hc = 20 \times 10^{-26}$ ,  $N_A = 6 \times 10^{23}$ ]
- Q.17 Calculate the threshold frequency of metal if the binding energy is  $198.9 \text{ KJ mol}^{-1}$  of electron.  
[Given :  $N_A = 6 \times 10^{23}$ ]
- Q.18 A photon of wavelength  $3000 \text{ \AA}$  strikes a metal surface, the work function of the metal being 2.20 eV. Calculate  
(i) the energy of the photon in eV  
(ii) the kinetic energy of the emitted photo electron and  
(iii) the velocity of the photo electron.
- Q.19 Photoelectrons are liberated by ultra violet light of wavelength  $2000 \text{ \AA}$  from a metallic surface for which the photoelectric threshold is  $4000 \text{ \AA}$ . Calculate maximum kinetic energy of photoelectrons.  $KE_{max} = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2}$
- Q.20 A metal was irradiated by light of frequency  $3.25 \times 10^{15} \text{ s}^{-1}$ . The photoelectron produced had its KE, 2 times the KE of the photoelectron which was produced when the same metal was irradiated with a light of frequency  $2.0 \times 10^{15} \text{ s}^{-1}$ . What is work function. [Given :  $N_A = 6 \times 10^{23}$ ]
- Q.21 When light of frequency  $3.2 \times 10^{16} \text{ Hz}$  is used to irradiate a metal surface the maximum kinetic energy of the emitted photoelectron is  $3/4$  of the energy of irradiating photon then the threshold frequency of the metal would be :
- Q.22 A light source of 320 watt emit monochromatic light of wavelength  $6200 \text{ \AA}$ . If all emitted photons are made to strike on metal plate of work function equal to 1.8 eV and quantum yield is 25% then photocurrent observe is
- Q.23 The K.E. of an electron emitted from tungsten surface is 3.06 eV. What voltage would be required to bring the electron to rest.

### BOHR'S MODEL

- Q.24 The radius of an orbit of hydrogen atom is 0.85 nm. Calculate the velocity of electron in this orbit.
- Q.25 The velocity of  $e^-$  in a certain Bohr orbit of the hydrogen atom bears the ratio 1:275 to the velocity of light. What is the quantum no. "n" of the orbit and the wave no. of the radiation emitted for the transition from the quatum state (n+1) to the ground state.

- Q.26 Calculate energy of electron which is moving in the orbit that has its radius, sixteen times the radius of first Bohr orbit for H-atom.
- Q.27 The energy of an excited H-atom is  $-3.4$  eV. Calculate angular momentum of  $e^-$  in the given orbit.
- Q.28 Estimate the difference in energy between I and II Bohr Orbit for a hydrogen atom.
- Q.29 Calculate the frequency of  $e^-$  in the first Bohr orbit in a H-atom.
- Q.30 If the average life time of an excited state of H atom is of order  $10^{-8}$  sec, estimate how many orbits an  $e^-$  makes when it is in the state  $n = 2$  and before it suffers a transition to  $n = 1$  state.
- Q.31 A single electron orbits around a stationary nucleus of charge  $+Ze$  where  $Z$  is atomic number and ' $e$ ' is the magnitude of the electric charge. The hydrogen like species required  $47.2$  eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find
- the value of  $Z$  and give the hydrogen like species formed.
  - the kinetic energy and potential energy of the electron in the first Bohr orbit.
- Q.32 H- atom is exposed to electromagnetic radiation of  $1028 \text{ \AA}$  and gives out induced radiations (radiations emitted when  $e^-$  returns to ground state). Calculate  $\lambda$  of induced radiations.
- Q.33 A stationary  $\text{He}^+$  ion emitted a photon corresponding to a first line of the Lyman series. The photon liberated electron from a stationary H atom in ground state. What is the velocity of electron.
- Q.34 Calculate the energy required to remove an  $e^-$  completely from  $n = 2$  orbit. What is the largest wavelength in cm of light that can be used to cause this transition.
- Q.35 Calculate the wavelength in angstrom of photon that is emitted when an  $e^-$  in Bohr orbit  $n=2$  returns to the orbit  $n=1$ .
- Q.36 The ionisation energy of the hydrogen atom is given to be  $13.6$  eV. A photon falls on a hydrogen atom which is initially in the ground state and excites it to the  $(n = 4)$  state. calculate the wavelength of the photon.
- Q.37 The angular momentum of an electron in a Bohr's orbit of H-atom is  $3.1652 \times 10^{-34} \text{ kg-m}^2/\text{sec}$ . Calculate the wavenumber in terms of Rydberg constant ( $R$ ) of the spectral line emitted when an electron falls from this level to the ground state.
- Q.38 A doubly ionised lithium atom is hydrogen like with atomic number  $z = 3$ . Find the wavelength of the radiation required to excite the electron in  $\text{Li}^{2+}$  from the first to the third Bohr orbit.
- Q.39 Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.
- Q.40 Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen.
- Q.41 The wavelength of a certain line in the Paschen series is  $1094.4 \text{ nm}$  of H-atom. What is the value of  $n_{\text{high}}$  for this line.

- Q.42 Wavelength of the Balmer  $H_\alpha$  line is 6565 Å. Calculate the wavelength of  $H_\beta$ , line of same hydrogen like atom.
- Q.43 Calculate the Rydberg constant  $R$  if  $He^+$  ions are known to have the wavelength difference between the first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7 nm.
- Q.44 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition,  $n=4$  to  $n=2$  of  $He^+$  spectrum.  $z=2$
- Q.45 Calculate the total energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum.
- Q.46 What will be the KE of photoelectron ejected by a metal upon irradiation with electromagnetic radiation of wavelength equal to that of the last line in Lyman series of  $He^+$  ion?  
workfunction of metal = 3.8 eV.

**DE BROGLIE HYPOTHESIS**

$$\frac{h}{p} = \lambda$$

$$p = mv$$

- Q.47 Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of 30 ms<sup>-1</sup>.
- Q.48 Two particles X and Y are in motion. If the wavelength associated with particle X is  $4 \times 10^{-8}$  m, calculate the wavelength associated with particle Y if its momentum is half of X.
- Q.49 Calculate the de-broglie wavelength associated with motion of earth (mass  $6 \times 10^{24}$  Kg) orbiting around the sun at a speed of  $3 \times 10^6$  m/s.  $\frac{h}{p} = \lambda$   $p = mv (3 \times 10^8)$
- Q.50 What should be the velocity of an electron so that its momentum becomes equal to that of a photon of wavelength 5200 Å.
- Q.51 What is de Broglie wavelength associated with an  $e^-$  accelerated through potential difference = 100 KV.

- Q.52 Through what potential difference must an electron pass to have a wavelength of 500 Å.

$$\sqrt{\frac{150}{100 \times 10^3}} \text{ Å}$$

- Q.53 To what effective potential a proton beam be subjected to give its protons a wavelength of  $1 \times 10^{-10}$  m.

- Q.54 An electron, practically at rest, is initially accelerated through a potential difference of 100 volts. It then has a de Broglie wavelength =  $\lambda_1$  Å. It then get retarded through 19 volts and then has a wavelength  $\lambda_2$

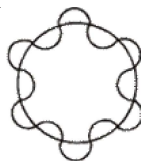
Å. A further retardation through 32 volts changes the wavelength to  $\lambda_3$  Å, What is  $\frac{\lambda_3 - \lambda_2}{\lambda_1}$

- Q.55 In a hydrogen atom, in transition of electron a photon of energy 2.55 eV is emitted, then calculate change in wavelength of the electron.

$$\lambda \approx \sqrt{\frac{150}{V}} \text{ Å}$$

potential

Q.56 The motion of electron present in all atoms of a sample of H(g) is as following :



If these electrons make transition from this orbit 'n' to ground state, calculate number of Paschen lines emitted.

Q.57 The de-Broglie wavelength associated with an electron in 4<sup>th</sup> orbit of hydrogen atom is  $a \times (\pi r_0)$  where  $r_0$  is radius of 1<sup>st</sup> orbit of hydrogen atom, find value of 'a'.

### **HEISENBERG'S UNCERTAINTY PRINCIPLE**

Q.58 A proton is accelerated to one-tenth of the velocity of light. If its velocity can be measured with a precision  $\pm 1\%$ . What must be its uncertainty in position.

Q.59 A base ball of mass 200 g is moving with velocity  $30 \times 10^2$  cm/s. If we can locate the base ball with an error equal in magnitude to the  $\lambda$  of the light used (5000 Å), how will the uncertainty in momentum be compared with the total momentum of base ball.

Q.60 An electron has a speed of 40 m/s, accurate up to 99.99%. What is the uncertainty in locating its position.

Q.61 The uncertainty in the location of circulating electron is equal to its de-Broglie wavelength. The minimum percent error in its measurement of velocity under this circumstance will be approximately

### **SCHRODINGER EQUATION / APPLICATION OF QUANTUM NUMBER**

Q.62 Mr. Santa has to decode a number "ABCDEF" where each alphabet is represented by a single digit. Suppose an orbital whose radial wave function is represented as

$$\Psi_{(r)} = k_1 \cdot e^{-r/k_2} (r^2 - 5k_3r + 6k_3^2)$$

From the following information given about each alphabet then write down the answers in the form of "ABCDEF", for above orbital.

Info A = Value of n where "n" is principal quantum number

Info B = No. of angular nodes

Info C = Azimuthal quantum number of subshell to orbital belongs

Info D = No. of subshells having energy between  $(n+5)s$  to  $(n+5)p$  where n is principal quantum number

Info E = Orbital angular momentum of given orbital.

Info F = Radial distance of the spherical node which is farthest from the nucleus

(Assuming :  $k_3 = 1$ )

Q.62 Calculate the distance of spherical nodes for '3s' orbital from nucleus?

$$R_{3s} = \frac{1}{9\sqrt{3}a_0^{3/2}} (6 - 6\sigma + \sigma^2) e^{-\frac{\sigma}{2}} \quad \text{where } \sigma = \frac{2r}{na_0}$$

Q.63 The difference between orbital angular momentum of a 2s and a 3d electron is

Q.64 The wave function of 2s electron is given by:  $\Psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-\left(2 - \frac{r}{a_0}\right)}$

If it has a node at  $r = r_0$ , find relation between  $r_0$  and  $a_0$ .

Q.65 Calculate magnitude of orbital angular momentum of an  $e^-$  that occupies 1s, 2s, 2p, 3d, 3p.

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## EXERCISE-2 (Objective Questions)

Single correct

- Q.1 The distance of closest approach of an  $\alpha$ -particle projected towards a nucleus with momentum  $p$  is  $r$ . What will be the distance of closest approach, when the momentum of projected  $\alpha$ -particle is  $2p$ ?
- (A)  $2r$  (B)  $4r$  (C)  $\frac{r}{2}$  (D)  $\frac{r}{4}$
- Q.2 The energy of electron is maximum at
- (A) Nucleus (B) Ground state  
(C) First excited state (D) Infinite distance from the nucleus
- Q.3 Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon
- (A)  $3s$  (B)  $2p$  (C)  $2s$  (D)  $1s$
- Q.4 Orbital angular momentum associated with  $2p$ -electron is :
- (A)  $\frac{\sqrt{2}h}{\pi}$  (B)  $0$  (C)  $\sqrt{6} \times \frac{h}{2\pi}$  (D)  $\frac{h}{\sqrt{2}\pi}$
- Q.5 The angular momentum of an electron in a certain orbit of  $\text{Li}^{+2}$  ion is  $3.15 \times 10^{-34}$  (in SI units). What will be the potential energy of electron in that orbit ?
- (A)  $-13.6 \text{ eV}$  (B)  $-27.2 \text{ eV}$  (C)  $+13.6 \text{ eV}$  (D)  $-53.4 \text{ eV}$
- Q.6 Which quantum number is not related with Schrodinger equation
- (A) Principal (B) Azimuthal (C) Magnetic (D) Spin
- Q.7 The shortest wavelength of He atom in Balmer series is  $x$ , then longest wavelength in the Paschen series of  $\text{Li}^{+2}$  is
- (A)  $\frac{36x}{5}$  (B)  $\frac{16x}{7}$  (C)  $\frac{9x}{5}$  (D)  $\frac{5x}{9}$
- Q.8 An electron, a proton and an alpha particle have kinetic energies of  $16E$ ,  $4E$  and  $E$  respectively. What is the qualitative order of their de Broglie wavelengths?
- (A)  $\lambda_e > \lambda_p = \lambda_\alpha$  (B)  $\lambda_p = \lambda_\alpha > \lambda_e$  (C)  $\lambda_p > \lambda_e > \lambda_\alpha$  (D)  $\lambda_\alpha < \lambda_e \gg \lambda_p$
- Q.9 The ratio of difference in wavelengths of  $1^{\text{st}}$  and  $2^{\text{nd}}$  lines of Lyman series in H-like atom to difference in wavelength for  $2^{\text{nd}}$  and  $3^{\text{rd}}$  lines of same series is:
- (A)  $2.5 : 1$  (B)  $3.5 : 1$  (C)  $4.5 : 1$  (D)  $5.5 : 1$
- Q.10 X-rays are emitted as the electrons deep within atoms having many electrons fall to lower energy states. What is the difference in energy between two levels if a transition between them gives rise to  $0.5 \text{ \AA}$  X-ray?
- (A)  $24.8 \text{ eV}$  (B)  $24.8 \text{ KeV}$  (C)  $24.8 \text{ MeV}$  (D) none of these
- Q.11 If radius of second stationary orbit (in Bohr's atom) is  $R$ . Then radius of third orbit will be
- (A)  $R/3$  (B)  $9R$  (C)  $R/9$  (D)  $2.25R$

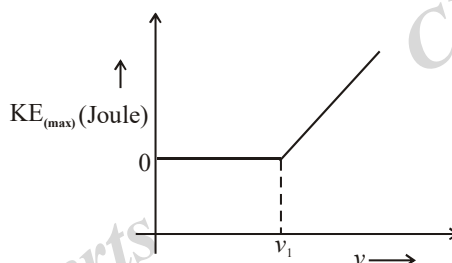
- Q.12 Wavelength of radiations emitted when an electron jumps from state A to C is  $3000 \text{ \AA}$  and it is  $6000 \text{ \AA}$  when the electron jumps from state B to state C. Wavelength of the radiations emitted when an electron jumps from state A to B will be  
 (A)  $6000 \text{ \AA}$  (B)  $3000 \text{ \AA}$  (C)  $4000 \text{ \AA}$  (D)  $2000 \text{ \AA}$
- Q.13 The ratio of wave length of photon corresponding to the  $\alpha$ -line of Lyman series in H-atom and  $\beta$ -line of Balmer series in  $\text{He}^+$  is  
 (A)  $1 : 1$  (B)  $1 : 2$  (C)  $1 : 4$  (D)  $3 : 16$
- Q.14 Three energy levels P, Q, R of a certain atom are such that  $E_P < E_Q < E_R$ . If  $\lambda_1, \lambda_2$  and  $\lambda_3$  are the wave length of radiation corresponding to transition  $R \rightarrow Q$ ;  $Q \rightarrow P$  and  $R \rightarrow P$  respectively. The correct relationship between  $\lambda_1, \lambda_2$  and  $\lambda_3$  is  
 (A)  $\lambda_1 + \lambda_2 = \lambda_3$  (B)  $\frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$  (C)  $\lambda_3 = \sqrt{\lambda_1 \lambda_2}$  (D)  $\frac{2}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$
- Q.15 The value of  $(n_2 + n_1)$  and  $(n_2^2 - n_1^2)$  for  $\text{He}^+$  ion in atomic spectrum are 4 and 8 respectively. The wavelength of emitted photon when electron jump from  $n_2$  to  $n_1$  is  
 (A)  $\frac{32}{9} R_H$  (B)  $\frac{9}{32} R_H$  (C)  $\frac{9}{32 R_H}$  (D)  $\frac{32}{9 R_H}$
- Q.16 Number of possible spectral lines which may be emitted in bracket series in H atom, if electrons present in  $9^{\text{th}}$  excited level returns to ground level, are  
 (A) 21 (B) 6 (C) 45 (D) 5
- Q.17 A mosquito of  $2 \text{ mg}$  is moving with a speed of  $(20 \pm 0.1) \text{ m/sec}$ . Uncertainty in its position is:  
 (A)  $2.64 \times 10^{-29} \text{ m}$  (B)  $2.64 \times 10^{-28} \text{ m}$  (C)  $2.64 \times 10^{-34} \text{ m}$  (D)  $2.64 \times 10^{-31} \text{ m}$
- Q.18 The wavelength associated with a golf weighing  $200 \text{ g}$  and moving at a speed of  $5 \text{ m/h}$  is of the order  
 (A)  $10^{-10} \text{ m}$  (B)  $10^{-20} \text{ m}$  (C)  $10^{-30} \text{ m}$  (D)  $10^{-40} \text{ m}$
- Q.19 The longest wavelength of  $\text{He}^+$  in Paschen series is " $m$ ", then shortest wavelength of  $\text{Be}^{+3}$  in Paschen series is (in terms of  $m$ ):  
 (A)  $\frac{5}{36} m$  (B)  $\frac{64}{7} m$  (C)  $\frac{53}{8} m$  (D)  $\frac{7}{64} m$
- Q.20 What is uncertainty in location of a photon of wavelength  $5000 \text{ \AA}$  if wavelength is known to an accuracy of  $1 \text{ pm}$ ?  
 (A)  $7.96 \times 10^{-14} \text{ m}$  (B)  $0.02 \text{ m}$  (C)  $3.9 \times 10^{-8} \text{ m}$  (D) none
- Q.21 Approximate De-Broglie wavelength ratio of  $\alpha$  particle with respect to proton is, if both are accelerated through same potential difference :  
 (A)  $\frac{1}{\sqrt{8}}$  (B)  $\frac{1}{2}$  (C) 2 (D)  $\sqrt{8}$



- Q.22 Electromagnetic radiations having  $\lambda = 310 \text{ \AA}$  are subjected to a metal sheet having work function = 12.8 eV. What will be the velocity of photoelectrons with maximum Kinetic Energy.  
 (A) 0, no emission will occur (B)  $2.18 \times 10^6 \text{ m/s}$   
 (C)  $2.18 \sqrt{2} \times 10^6 \text{ m/s}$  (D)  $8.72 \times 10^6 \text{ m/s}$
- Q.23 Assuming Heisenberg Uncertainty Principle to be true what could be the minimum uncertainty in de-broglie wavelength of a moving electron accelerated by Potential Difference of 6 V whose uncertainty in position is  $\frac{7}{22} \text{ n.m.}$   
 (A) 6.25  $\text{\AA}$  (B) 6  $\text{\AA}$  (C) 0.625  $\text{\AA}$  (D) 0.3125  $\text{\AA}$
- Q.24 When an excited hydrogen atom returned to its ground state, some visible quanta were observed along with other quanta. Which of the following transitions must have occurred?  
 (A)  $2 \rightarrow 1$  (B)  $3 \rightarrow 1$  (C)  $3 \rightarrow 1$  (D)  $4 \rightarrow 1$
- Q.25 A photon of 300 nm is absorbed by a gas and then re-emits two photons. One re-emitted photon has wavelength 496 nm, the wavelength of second re-emitted photon is :  
 (A) 759 (B) 857 (C) 957 (D) 657
- Q.26 Which has the highest specific charge?  
 (A)  $\text{Na}^+$  (B)  $\text{Mg}^{+2}$  (C)  $\text{Al}^{3+}$  (D)  $\text{Si}^{4+}$
- Q.27 According to Bohr's atomic theory, which of the following relations is/are incorrect?  
 (A) Kinetic energy of electron  $\propto \frac{Z^2}{n^2}$   
 (B) The product of velocity of electron and the principal quantum number  $\propto Z^2$   
 (C) Frequency of revolution of the electron in an orbit  $\propto \frac{Z^2}{n^3}$   
 (D) Coulombic force of attraction on the electron  $\propto \frac{Z^3}{n^4}$
- Q.28 A mono electronic species in energy level with energy 'X' was provided with excess of energy so that it jumps to higher energy level with energy Y. If it can emit 6 wavelengths originated from all possible transition between these group levels, then which of the following relation is correct:  
 (Here n is the principal quantum number of energy level X) :  
 (A)  $X/Y = (n-1)^2$  (B)  $X/Y = 1 + 3/n$   
 (C)  $\sqrt{X/Y} = 1 + 3/n$  (D)  $X/Y = n/6$
- Q.29 The transition from the state  $n = 4$  to  $n = 3$  in a  $\text{He}^+$  ion results in ultraviolet radiation. Infrared radiation will be obtained in the transition from :  
 (A)  $n = 2 \rightarrow n = 1$  (B)  $n = 3 \rightarrow n = 2$  (C)  $n = 4 \rightarrow n = 2$  (D)  $n = 5 \rightarrow n = 4$
- Q.30 The angular momentum of an electron of H - atom is proportional to :  
 (A)  $r^2$  (B)  $\frac{1}{r}$  (C)  $\sqrt{r}$  (D)  $\frac{1}{\sqrt{r}}$

- Q.31 Wavelength of the de-Broglie wave of an electron revolving in the sixth orbit of the hydrogen atom is : ( $r_0$  is the Bohr's radius =  $0.529 \text{ \AA}$ )  
 (A)  $\pi r_0$  (B)  $12\pi r_0$  (C)  $6\pi r_0$  (D)  $24\pi r_0$

- Q.32 Graph between kinetic energy of photoelectron  $KE_{(\max)}$  Vs frequency ( $\nu$ ) of an incident photon is given when light is incident on a metal plate during photoelectric experiment :



Wavelength of light corresponding to frequency  $\nu_1$  is  $200 \text{ nm}$ . If monochromatic light of wavelength  $100 \text{ nm}$  is incident on metal plate then  $K.E._{(\max)}$  of ejected photoelectron is :

- (A)  $1 \times 10^{-27} \text{ J}$  (B)  $9.9 \times 10^{-17} \text{ J}$  (C)  $9.9 \times 10^{-19} \text{ J}$  (D)  $1 \times 10^{-22} \text{ J}$
- Q.33 The energy of an electron in the first Bohr orbit of H atom is  $-13.6 \text{ eV}$ . The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is/are :

- (A)  $-3.4 \text{ eV}$  (B)  $-4.2 \text{ eV}$  (C)  $-6.8 \text{ eV}$  (D)  $+6.8 \text{ eV}$

- Q.34 The number of nodal planes in a  $p_x$  orbital is:

- (A) one (B) two (C) three (D) zero

- Q.35 The quantum numbers  $+1/2$  and  $-1/2$  for the electron spin represent:

- (A) rotation of the electron in clockwise and anticlockwise direction respectively.  
 (B) rotation of the electron in anticlockwise and clockwise direction respectively.  
 (C) magnetic moment of the electron pointing up and down respectively.  
 (D) two quantum mechanical spin states which have no classical analogue.

- Q.36 Two different photons of energies,  $1 \text{ eV}$  and  $2.5 \text{ eV}$ , fall on two identical metal plates having work function  $0.5 \text{ eV}$ , Then the ratio of maximum KE of the electrons emitted from the two surface is -

- (A)  $1 : 2$  (B)  $1 : 4$  (C)  $2 : 1$  (D)  $4 : 1$

- Q.37 An atom has a mass of  $0.02 \text{ kg}$  & uncertainty in its velocity is  $9.218 \times 10^{-6} \text{ m/s}$  then uncertainty in position is : ( $h = 6.626 \times 10^{-34} \text{ J-s}$ )

- (A)  $2.86 \times 10^{-28} \text{ m}$  (B)  $2.86 \times 10^{-32} \text{ cm}$  (C)  $1.5 \times 10^{-27} \text{ m}$  (D)  $3.9 \times 10^{-10} \text{ m}$

- Q.38 Energy of H-atom in the ground state is  $-13.6 \text{ eV}$ , Hence energy in the second excited state is -

- (A)  $-6.8 \text{ eV}$  (B)  $-3.4 \text{ eV}$  (C)  $-1.51 \text{ eV}$  (D)  $-4.3 \text{ eV}$

- Q.39 Uncertainty in position of a particle of  $25 \text{ g}$  in space is  $10^{-5} \text{ m}$ . Hence uncertainty in velocity ( $\text{ms}^{-1}$ ) is (Planck's constant  $h = 6.6 \times 10^{-34} \text{ Js}$ )

- (A)  $2.1 \times 10^{-28}$  (B)  $2.1 \times 10^{-34}$  (C)  $0.5 \times 10^{-34}$  (D)  $5.0 \times 10^{-24}$

- Q.40 In Bohr series of lines of hydrogen spectrum, third line from the red end corresponds to where one of the following inter-orbit jumps of electron for Bohr orbits in an atom of hydrogen.
- (A)  $4 \rightarrow 1$                       (B)  $2 \rightarrow 5$                       (C)  $3 \rightarrow 2$                       (D)  $5 \rightarrow 2$

### Comprehension

#### Paragraph for question nos. 41 to 43

The French physicist Louis de Broglie in 1924 postulated that matter, like radiation, should exhibit a dual behaviour. He proposed the following relationship between the wavelength  $\lambda$  of a material particle, its linear momentum  $p$  and planck constant  $h$ .

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

The de Broglie relation implies that the wavelength of a particle should decrease as its velocity increases. It also implies that for a given velocity heavier particles should have shorter wavelength than lighter particles. The waves associated with particles in motion are called matter waves or de Broglie waves. These waves differ from the electromagnetic waves as they

- (i) have lower velocities
- (ii) have no electrical and magnetic fields and
- (iii) are not emitted by the particle under consideration.

The experimental confirmation of the de Broglie relation was obtained when Davisson and Germer, in 1927, observed that a beam of electrons is diffracted by a nickel crystal. As diffraction is a characteristic property of waves, hence the beam of electron behaves as a wave, as proposed by de Broglie.

Werner Heisenberg considered the limits of how precisely we can measure properties of an electron or other microscopic particle like electron. He determined that there is a fundamental limit of how closely we can measure both position and momentum. The more accurately we measure the momentum of a particle, the less accurately we can determine its position. The converse is also true. This is summed up in what we now call the "Heisenberg uncertainty principle: It is impossible to determine simultaneously and precisely both the momentum and position of a particle. The product of uncertainty in the position,

$\Delta x$  and the uncertainty in the momentum  $\Delta(mv)$  must be greater than or equal to  $\frac{h}{4\pi}$ . i.e.

$$\Delta x \Delta(mv) \geq \frac{h}{4\pi}$$

- Q.41 The correct order of wavelength of Hydrogen ( ${}_1H^1$ ), Deuterium ( ${}_1H^2$ ) and Tritium ( ${}_1H^3$ ) moving with same kinetic energy is
- (A)  $\lambda_H > \lambda_D > \lambda_T$                       (B)  $\lambda_H = \lambda_D = \lambda_T$                       (C)  $\lambda_H < \lambda_D < \lambda_T$                       (D)  $\lambda_H < \lambda_D > \lambda_T$
- Q.42 The transition, so that the de-Broglie wavelength of electron becomes 3 times of its initial value in  $He^+$  ion will be
- (A)  $2 \rightarrow 5$                       (B)  $3 \rightarrow 2$                       (C)  $2 \rightarrow 6$                       (D)  $1 \rightarrow 2$
- Q.43 If the uncertainty in velocity & position is same, then the uncertainty in momentum will be
- (A)  $\sqrt{\frac{hm}{4\pi}}$                       (B)  $m\sqrt{\frac{h}{4\pi}}$                       (C)  $\sqrt{\frac{h}{4\pi m}}$                       (D)  $\frac{1}{m}\sqrt{\frac{h}{4\pi}}$

**Paragraph for question nos. 44 to 47**

The only electron in the hydrogen atom resides under ordinary conditions on the first orbit. When energy is supplied, the electron moves to higher energy orbit depending on the amount of energy absorbed. When this electron returns to any of the lower orbits, it emits energy. Lyman series is formed when the electron returns to the lowest orbit while Balmer series is formed when the electron returns to second orbit. Similarly, Paschen, Brackett and Pfund series are formed when electron returns to the third, fourth and fifth orbits from higher energy orbits respectively.

Maximum number of lines produced when an electron jumps from  $n$ th level to ground level is equal

to  $\frac{n(n-1)}{2}$ . For example, in the case of  $n=4$ , number of lines produced is 6. ( $4 \rightarrow 3$ ,  $4 \rightarrow 2$ ,  $4 \rightarrow 1$ ,  $3 \rightarrow 2$ ,  $3 \rightarrow 1$ ,  $2 \rightarrow 1$ ). When an electron returns from  $n_2$  to  $n_1$  state, the number of lines in the spectrum will be equal to

$$\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

If the electron comes back from energy level having energy  $E_2$  to energy level having energy  $E_1$ , then the difference may be expressed in terms of energy of photon as:

$$E_2 - E_1 = \Delta E, \lambda = \frac{hc}{\Delta E}$$

Since  $h$  and  $c$  are constants,  $\Delta E$  corresponds to definite energy; thus each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom.

Wave number of line is given by the formula  $\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ .

where  $R$  is a Rydberg's constant ( $R = 1.1 \times 10^7 \text{ m}^{-1}$ )

- Q.44 The energy photon emitted corresponding to transition  $n=3$  to  $n=1$  is  **$[h = 6 \times 10^{-34} \text{ J-sec.}]$**   
 (A)  $1.76 \times 10^{-18} \text{ J}$  (B)  $1.98 \times 10^{-18} \text{ J}$  (C)  $1.76 \times 10^{-17} \text{ J}$  (D) None of these
- Q.45 In a collection of H-atom, electrons make transition from 5<sup>th</sup> excited state to 2<sup>nd</sup> excited state then maximum number of different types of photons observed are  
 (A) 3 (B) 4 (C) 6 (D) 15
- Q.46 The difference in the wavelength of the 1<sup>st</sup> line of Lyman series and 2<sup>nd</sup> line of Balmer series in a hydrogen atom is  
 (A)  $\frac{9}{2R}$  (B)  $\frac{4}{R}$  (C)  $\frac{88}{15R}$  (D) None
- Q.47 The wave number of electromagnetic radiation emitted during the transition of electron in between two levels of  $\text{Li}^{2+}$  ion whose principal quantum numbers sum is 4 and difference is 2 is  
 (A)  $3.5 R$  (B)  $4 R$  (C)  $8 R$  (D)  $\frac{8}{9} R$

**Paragraph for question nos. 48 to 50**

The wave function,  $\psi_{n,l,m}$  is a mathematical function whose value depends upon spherical polar coordinates  $(r, \theta, \phi)$  of the electron and characterized by the quantum numbers  $n, l$  and  $m_l$ . Here  $r$  is distance from nucleus,  $\theta$  is colatitude and  $\phi$  is azimuth. In the mathematical functions given in the Table,  $Z$  is atomic number and  $a_0$  is Bohr radius.

**Column 1****Column 2****Column 3**

(I) 2s orbital      (i)  $\psi(r) \propto \left(\frac{Z}{a_0}\right)^{3/2} r^2 e^{-Zr/3a_0}$

(P) one angular node

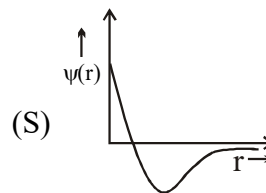
(II) 2p orbital      (ii)  $\psi(\theta, \phi) \propto \sqrt{\frac{1}{4\pi}}$

(Q) Probability density changes on changing angle.

(III)  $3p_z$  orbital      (iii)  $\psi(r) \propto \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$

(R) One radial node

(IV)  $3d_{xy}$  orbital      (iv)  $\psi(r) \propto \left(\frac{Z}{a_0}\right)^{3/2} \left(4 - \frac{2Zr}{3a_0}\right) \left(\frac{r}{3}\right) e^{-Zr/3a_0}$

Q.48 Which of the following is **correct** combination ?

(A) (I) (iii) (P)

(B) (I) (ii) (S)

(C) (I) (iv) (S)

(D) (II) (ii) (P)

Q.49 Which of the following is **correct** combination ?

(A) (IV) (iv) (R)

(B) (III) (ii) (S)

(C) (III) (iii) (R)

(D) (III) (iv) (P)

Q.50 Which of the following is **correct** combination?

(A) (II) (ii) (R)

(B) (II) (iv) (P)

(C) (IV) (iii) (Q)

(D) (IV) (i) (Q)

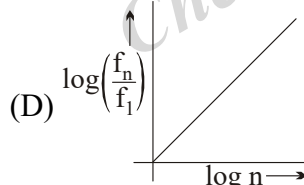
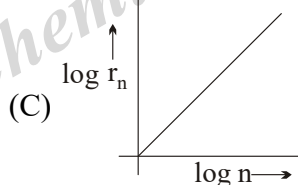
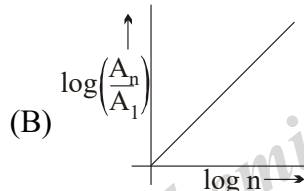
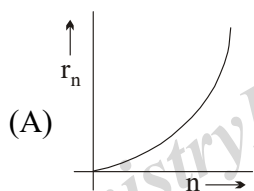
**Assertion Reason**

- Q.51 **Statement-1:** Energy emitted when an electron jump from  $5 \rightarrow 2$  (energy level) is less than when an electron jump from  $2 \rightarrow 1$  in all 'H' like atom.  
**Statement-2:** The [total energy difference] between 1<sup>st</sup> & 2<sup>nd</sup> energy level is greater than that of any two energy level provided level '1' is not part of those two energy levels.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- Q.52 **Statement-1:** Emitted radiations will fall in visible range when an electron jump from higher level to  $n = 2$  in  $\text{Li}^{+2}$  ion.  
**Statement-2:** Balmer series radiations belong to visible range in H-atoms.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- Q.53 **Statement-1 :** Radial part of wave function of  $4p_x$  and  $3p_y$  are not same.  
**Statement-2 :** Radial part of wave functions depends on  $l$  &  $m$  and angular part of wave function depends on  $n$  &  $l$ .  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**More than one may be correct**

- Q.54 **Correct** statement(s) regarding  $3P_y$  orbital is/are  
 (A) Angular part of wave function is independent of angles ( $\theta$  and  $\phi$ )  
 (B) No. of maxima when a curve is plotted between  $4\pi r^2 R^2(r)$  vs  $r$  are '2'  
 (C) 'xz' plane acts as nodal plane  
 (D) Magnetic quantum number must be '-1'
- Q.55 In a H-like sample electrons make transition from 4<sup>th</sup> excited state to 2<sup>nd</sup> state then  
 (A) 10 different spectral lines are observed  
 (B) 6 different spectral lines are observed  
 (C) Number of lines belonging to the Balmer series is 3.  
 (D) Number of lines belonging to the Paschen series is 2.
- Q.56 Choose the incorrect statement(s):  
 (A) The order of wavelength is  
     Micro waves > Radio waves > IR waves > visible waves > UV waves  
 (B) The order of Bohr radius is ( $r_n$  : where  $n$  is orbit number for a given atom)  
      $r_1 < r_2 < r_3 < r_4$   
 (C) The order of total energy is ( $E_n$  : where  $n$  is orbit number for a given atom)  
      $E_1 > E_2 > E_3 > E_4$   
 (D) The order of velocity of electron in H,  $\text{He}^+$ ,  $\text{Li}^+$ ,  $\text{Be}^{3+}$  species in second Bohr orbit is  
      $\text{Be}^{3+} > \text{Li}^{+2} > \text{He}^+ > \text{H}$

Q.57 If, in hydrogen atom, radius of  $n^{\text{th}}$  Bohr orbit is  $r_n$ , frequency of revolution of electron in  $n^{\text{th}}$  orbit is  $f_n$  and area enclosed by  $n^{\text{th}}$  orbit is  $A_n$ , which of the following graphs is / are correct?



Q.58 Which is / are **correct** statement.

- (A) The difference in angular momentum associated with the electron present in consecutive orbits of H-atom is  $(n-1) \frac{h}{2\pi}$
- (B) Energy difference between energy levels will be changed if, P.E. at infinity assigned value other than zero.
- (C) Frequency of spectral line in a H-atom is in the order of  $(2 \rightarrow 1) < (3 \rightarrow 1) < (4 \rightarrow 1)$
- (D) On moving away from the nucleus, kinetic energy of electron decreases.

Q.59 If uncertainty in velocity is  $6.62 \times 10^{-2} \text{ m/s}$  for a particle of mass of  $\frac{0.05}{\pi} \text{ gm}$ . Its uncertainty in position may be

(A)  $0.5 \times 10^{-18}$

(B)  $10^{-18}$

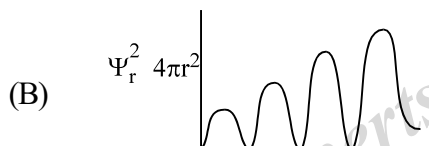
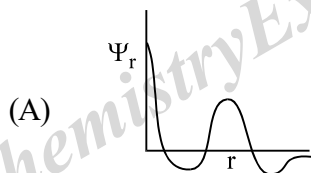
(C)  $0.8 \times 10^{-18}$

(D)  $0.5 \times 10^{-17}$

## [MATRIX TYPE]

Q.60 Column I & column II contain data on Schrodinger Wave-Mechanical model, where symbols have their usual meanings. Match the columns.

## Column I



(C)  $\Psi(\theta, \phi) = K$  (independent of  $\theta$  &  $\phi$ )

(D) atleast one angular node is present

## Column II (Type of orbital)

(P) 4s

(Q) any of the 5p orbital

(R) 3s

(S) any of the 6d orbital

Q.61

## Column-I

(A) Electron moving in 2<sup>nd</sup> orbit in He<sup>+</sup> ion (P) electron is

(B) Electron moving in 3<sup>rd</sup> orbit in H-atom (Q)

(C) Electron moving in 1<sup>st</sup> orbit in Li<sup>+2</sup> ion (R)

(D) Electron moving in 2<sup>nd</sup> orbit is Be<sup>+3</sup> ion (S)

## Column-II

Radius of orbit in which moving is 0.529 Å

Total energy of electron is  $(-13.6 \times 9 \text{ eV})$

Velocity of electron is  $\frac{2.188 \times 10^6}{3} \text{ m/sec}$

De-broglie wavelength of electron is  $\sqrt{\frac{150}{13.6}} \text{ Å}$



**ANSWER KEY****EXERCISE - 1**

|      |                                                                |      |                                                                                                          |
|------|----------------------------------------------------------------|------|----------------------------------------------------------------------------------------------------------|
| Q.1  | $2.1 \times 10^{-13} \text{ J}, 3.4 \times 10^{-14} \text{ m}$ | Q.2  | $1.39 \times 10^8 \text{ C/kg}$                                                                          |
| Q.3  | $8.64 \times 10^6 \text{ eV}$                                  | Q.4  | $6.3 \times 10^6 \text{ m/s}$                                                                            |
| Q.5  | $3.37 \times 10^{-10}$                                         | Q.6  | $621.1 \text{ eV}$                                                                                       |
| Q.7  | $20,000$                                                       | Q.8  | $28 \text{ photons}$                                                                                     |
| Q.9  | $0.5080$                                                       | Q.10 | $3 \times 10^{22}$                                                                                       |
| Q.11 | $4.96 \times 10^{-7} \text{ m}$                                | Q.12 | $8.68 \%$                                                                                                |
| Q.13 | $10^{22}$                                                      | Q.14 | $1.56 \times 10^{16}$                                                                                    |
| Q.15 | $27.2 \times 10^{18}$                                          | Q.16 | $500 \text{ KJ/mol}$                                                                                     |
| Q.17 | $5 \times 10^{14} \text{ s}^{-1}$                              | Q.18 | (1) $4.1235 \text{ eV}$ , (ii) $3.08 \times 10^{-19} \text{ J}$ (iii) $8.22 \times 10^5 \text{ ms}^{-1}$ |
| Q.19 | $4.969 \times 10^{-19} \text{ J}$                              | Q.20 | $298.35 \text{ KJ/mol}$                                                                                  |
| Q.21 | $8 \times 10^{15} \text{ Hz}$                                  | Q.22 | $40 \text{ Amp}$                                                                                         |
| Q.23 | $3.06 \text{ V}$                                               | Q.24 | $5.44 \times 10^5 \text{ m/s}$                                                                           |
| Q.25 | $2 ; 9.75 \times 10^4 \text{ cm}^{-1}$                         | Q.26 | $-1.36 \times 10^{-19} \text{ J}$                                                                        |
| Q.27 | $h/\pi$                                                        | Q.28 | $10.2 \text{ eV}$                                                                                        |
| Q.29 | <u><math>6530 \times 10^{12} \text{ Hz}</math></u>             | Q.30 | $8 \times 10^6$                                                                                          |
| Q.31 | $340 \text{ eV}, -680 \text{ eV}$                              | Q.32 | $6563 \text{ \AA} ; 1216 \text{ \AA} ; 1028 \text{ \AA}$                                                 |
| Q.33 | $3.09 \times 10^8 \text{ cm/sec}$                              | Q.34 | $5.425 \times 10^{-12} \text{ ergs}, 3.7 \times 10^{-5} \text{ cm}$                                      |
| Q.35 | $1220 \text{ \AA}$                                             | Q.36 | $973.5 \text{ \AA}$                                                                                      |
| Q.37 | $R \left( \frac{8}{9} \right)$                                 | Q.38 | $114 \text{ \AA}$                                                                                        |
| Q.39 | $972.8 \text{ \AA}$                                            | Q.40 | $27425 \text{ cm}^{-1}$                                                                                  |
| Q.41 | $6$                                                            | Q.42 | $4863 \text{ \AA}$                                                                                       |
| Q.43 | $1.096 \times 10^7 \text{ m}^{-1}$                             | Q.44 | $n_1=1, n_2=2$                                                                                           |
| Q.45 | $1.82 \times 10^5 \text{ J/mol}$                               | Q.46 | $50.6 \text{ eV}$                                                                                        |
| Q.47 | $2.2 \times 10^{-34} \text{ m}$                                | Q.48 | $8 \times 10^{-8} \text{ m}$                                                                             |
| Q.49 | $3.68 \times 10^{-65} \text{ m}$                               | Q.50 | $1400 \text{ m/s}$                                                                                       |
| Q.51 | $3.88 \text{ pm}$                                              | Q.52 | $6.03 \times 10^{-4} \text{ Volt}$                                                                       |
| Q.53 | $0.0826 \text{ Volts}$                                         | Q.54 | $20/63$                                                                                                  |
| Q.55 | $6.64 \text{ \AA}$                                             | Q.56 | $3$                                                                                                      |
| Q.57 | $8$                                                            | Q.58 | $1.05 \times 10^{-13} \text{ m}$                                                                         |
| Q.59 | $0.0144 \text{ m}$                                             | Q.60 | $8$                                                                                                      |

Q.61 300303      Q.62  $\frac{9+3\sqrt{3}}{2}a_0, \frac{9-3\sqrt{3}}{2}a_0$       Q.63  $\sqrt{6}\hbar$

Q.64  $r_0 = 2a_0$       Q.65  $0; 0; \sqrt{2}\frac{h}{2\pi}; \sqrt{6}\frac{h}{2\pi}; \sqrt{2}\frac{h}{2\pi}$

**EXERCISE - 2**

- |                                          |                                 |         |           |          |
|------------------------------------------|---------------------------------|---------|-----------|----------|
| Q.1 D                                    | Q.2 D                           | Q.3 D   | Q.4 D     | Q.5 B    |
| Q.6 D                                    | Q.7 B                           | Q.8 A   | Q.9 B     | Q.10 B   |
| Q.11 D                                   | Q.12 A                          | Q.13 A  | Q.14 B    | Q.15 C   |
| Q.16 B                                   | Q.17 B                          | Q.18 C  | Q.19 D    | Q.20 B   |
| Q.21 A                                   | Q.22 C                          | Q.23 C  | Q.24 A    | Q.25 A   |
| Q.26 D                                   | Q.27 B                          | Q.28 C  | Q.29 D    | Q.30 C   |
| Q.31 B                                   | Q.32 C                          | Q.33 A  | Q.34 A    | Q.35 D   |
| Q.36 B                                   | Q.37 A                          | Q.38 C  | Q.39 A    | Q.40 D   |
| Q.41 A                                   | Q.42 C                          | Q.43 A  | Q.44 A    | Q.45 C   |
| Q.46 B                                   | Q.47 C                          | Q.48 B  | Q.49 D    | Q.50 D   |
| Q.51 A                                   | Q.52 D                          | Q.53 C  | Q.54 BC   | Q.55 BCD |
| Q.56 AC                                  | Q.57 AB                         | Q.58 CD | Q.59 ABCD |          |
| Q.60 (A) P, (B) P,Q,S, (C) P, R (D) Q, S | Q.61 (A) S, (B) R, (C) Q, (D) P |         |           |          |

# EXERCISE-ZERO

## Determination of Oxidation number

**Q1** Determine the O.N. of the underlined elements in following species :

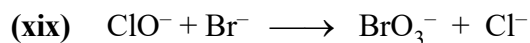
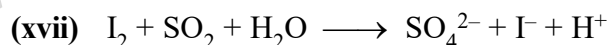
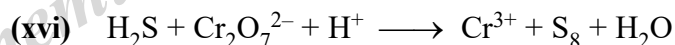
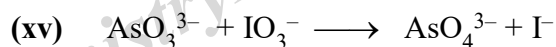
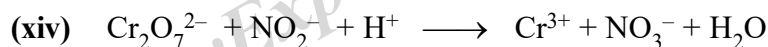
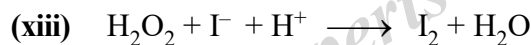
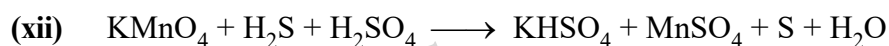
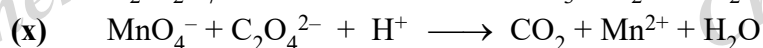
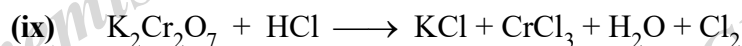
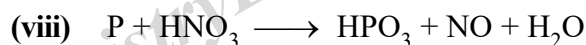
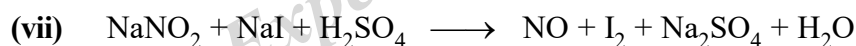
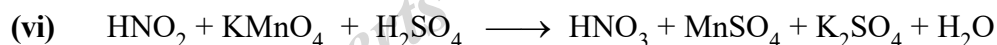
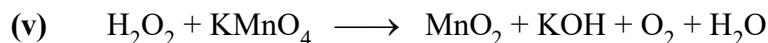
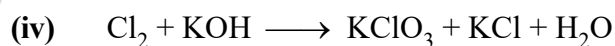
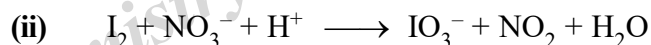
- |                                              |                                                   |                                                |                                               |
|----------------------------------------------|---------------------------------------------------|------------------------------------------------|-----------------------------------------------|
| (1) $\text{H}\underline{\text{F}}$           | (2) $\underline{\text{Fe}}\text{O}$               | (3) $\underline{\text{Na}}_2\text{O}$          | (4) $\underline{\text{C}}_2\text{H}_6$        |
| (5) $\underline{\text{Pb}}\text{O}_2$        | (6) $\text{H}\underline{\text{N}}\text{O}_3$      | (7) $\text{H}_2\underline{\text{S}}\text{O}_4$ | (8) $\underline{\text{N}}\text{H}_4\text{OH}$ |
| (9) $\underline{\text{N}}\text{H}_3$         | (10) $\underline{\text{N}}_3\text{H}$             | (11) $\underline{\text{Cu}}\text{S}$           | (12) $\underline{\text{Cu}}_2\text{S}$        |
| (13) $\underline{\text{N}}_2\text{O}_5$      | (14) $\text{H}_2\underline{\text{S}}_2\text{O}_3$ | (15) $\underline{\text{Mn}}\text{O}_4^-$       | (16) $\underline{\text{Mn}}\text{O}_4^{2-}$   |
| (17) $\underline{\text{C}}_2\text{O}_4^{2-}$ | (18) $\underline{\text{Cr}}_2\text{O}_7^{2-}$     | (19) $\underline{\text{Cr}}\text{O}_4^{2-}$    | (20) $\underline{\text{Zn}}\text{O}_2^{2-}$   |

**Q1** Determine the O.N. of the underlined elements in following species :

- |                                                                                                   |                                                                                      |                                                          |                                                              |
|---------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------|--------------------------------------------------------------|
| (1) $\underline{\text{Fe}}_3\text{O}_4$                                                           | (2) $\underline{\text{K}}\text{O}_2$                                                 | (3) $\text{Na}_2\underline{\text{S}}_4\text{O}_6$        | (4) $\underline{\text{C}}_2\text{H}_5\text{OH}$              |
| (5) $\underline{\text{Fe}}\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ | (6) $\underline{\text{Na}}_2\text{O}_2$                                              | (7) $\underline{\text{Fe}}\text{S}_2$                    |                                                              |
| (8) $\text{CaO}\underline{\text{Cl}}_2$                                                           | (9) $\text{Ca}(\underline{\text{OCl}})_2$                                            | (10) $\underline{\text{Cr}}\text{O}_5$                   | (11) $(\underline{\text{N}}\text{H}_4)_2\text{SO}_4$         |
| (12) $\text{Na}_2\underline{\text{S}}_2\text{O}_8$                                                | (13) $\text{H}\underline{\text{C}}\text{N}$                                          | (14) $\text{H}\underline{\text{N}}\underline{\text{C}}$  | (15) $\text{Ba}[\text{H}_2\underline{\text{P}}\text{O}_2]_2$ |
| (16) $\underline{\text{Os}}\text{O}_4$                                                            | (17) $\text{Na}\underline{\text{H}}$                                                 | (18) $\text{CH}_3\underline{\text{S}}\text{O}_3\text{H}$ | (19) $\text{Ba}_2\underline{\text{Xe}}\text{O}_6$            |
| (20) $\text{Ba}(\underline{\text{SCN}})_2$                                                        | (21) $\text{K}[\underline{\text{Co}}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_3)_2]$ | (22) $\text{K}_4\underline{\text{P}}_2\text{O}_7$        |                                                              |
| (23) $\underline{\text{Cr}}\text{O}_2\text{Cl}_2$                                                 | (24) $\underline{\text{Mn}}_3\text{O}_4$                                             | (25) $\text{Ca}(\underline{\text{ClO}}_2)_2$             | (26) $\text{H}_2\underline{\text{S}}\text{O}_5$              |
| (27) $\underline{\text{Fe}}_{0.93}\text{O}$                                                       |                                                                                      |                                                          |                                                              |

**EXERCISE-1 (Subjective Questions)**
**Balancing of Redox reactions**

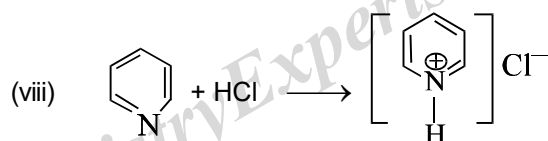
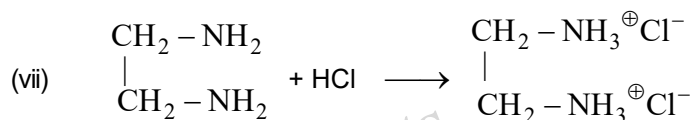
Q.1 Balance following reactions :



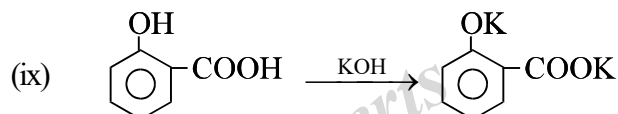
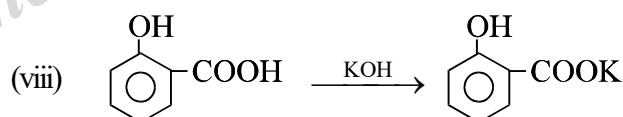
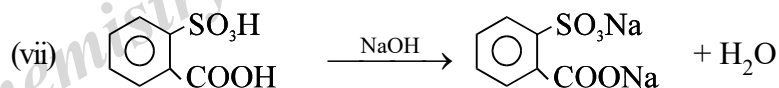
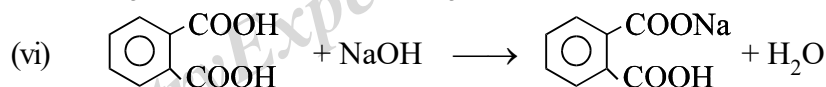
N-factor calculations

 Q.2 Find the **N-factor** of base in following reactions

- (i)  $\text{Al(OH)}_3 + \text{HCl} \longrightarrow \text{Al(OH)Cl}_2 + \text{H}_2\text{O}$   
 (ii)  $\text{Al(OH)}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Al(OH)(HSO}_4)_2 + \text{H}_2\text{O}$   
 (iii)  $\text{MgAl(OH)}_5 + \text{HCl} \longrightarrow \text{MgCl} + \text{AlCl}_3 + \text{H}_2\text{O}$   
 (iv)  $\text{Ba(OH)}_2 + \text{HCl} \longrightarrow \text{Ba(OH)Cl} + \text{H}_2\text{O}$   
 (v)  $\text{Ba(OH)}_2 + \text{HCl} \longrightarrow \text{BaCl}_2 + \text{H}_2\text{O}$   
 (vi)  $\text{R-NH}_2 + \text{HCl} \longrightarrow \text{R-NH}_3^+ \text{Cl}^-$


 Q.3 Find the **N-factor** of acid in following reactions

- (i)  $\text{H}_3\text{SbO}_4 \xrightarrow{\text{KOH}} \text{KH}_2\text{SbO}_4 + \text{H}_2\text{O}$   
 (ii)  $\text{H}_3\text{SbO}_4 + \text{KOH} \longrightarrow \text{K}_2\text{HSbO}_4 + \text{H}_2\text{O}$   
 (iii)  $\text{H}_2\text{SO}_4 + \text{KOH} \longrightarrow \text{KHSO}_4 + \text{H}_2\text{O}$   
 (iv)  $\text{H}_2\text{SO}_4 + \text{KOH} \longrightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$   
 (v)  $\text{H}_3\text{PO}_4 + \text{NaOH} \longrightarrow \text{Na}_3\text{PO}_4 + \text{H}_2\text{O}$


 Q.4 Find the **N-factor** of underlined species in following reactions :

- (a)  $\underline{\text{N}_2\text{H}_4} \longrightarrow \text{N}_2 + \text{NH}_3$  (b)  $\underline{\text{KMnO}_4} \longrightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$   
 (c)  $\underline{\text{CH}_4} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$  (d)  $\underline{\text{Cl}_2} \longrightarrow \text{ClO}_4^- + \text{Cl}^-$   
 (e)  $\underline{\text{As}_2\text{S}_3} + \underline{\text{Mn(NO}_3)_2} + \text{K}_2\text{CO}_3 \longrightarrow \text{K}_3\text{AsO}_4 + \text{K}_2\text{SO}_4 + \text{K}_2\text{MnO}_4 + \text{NO} + \text{CO}_2$   
 (f)  $\underline{\text{Bi}_2\text{S}_3} \longrightarrow \text{Bi}^{+5} + \text{S}$  (g)  $\underline{\text{Ba(SCN)}_2} \longrightarrow \text{BaSO}_4 + \text{HCN}$   
 (h)  $\underline{3\text{Mn}^{+7}} \longrightarrow 2\text{Mn}^{+2} + \text{Mn}^{+4}$  (i)  $\underline{\text{K}_4\text{Fe(CN)}_6} \longrightarrow \text{Fe}^{3+} + \text{CO}_2 + \text{NO}_3^-$

- Q.5 Calculate normality of a salt solution [of a metal sulphate] having concentration 21.6 % w/v if its superoxide has 16 % by mass of oxygen.

**Acid Base Titration**

- Q.6 Calculate volume of 1N  $\text{H}_3\text{PO}_4$  required to react with 20ml 2N  $\text{Ca}(\text{OH})_2$  solution.
- Q.7 Calculate volume of 1N  $\text{H}_2\text{SO}_4$  required to react with 20ml 1M  $\text{Al}(\text{OH})_3$  solution.
- Q.8 Calculate volume of 0.4 M NaOH required to react with following mixture  
 $\text{HCl}$  (1 mol) +  $\text{H}_2\text{SO}_4$  (2 mol)
- Q.9 Calculate volume of 0.2 M  $\text{H}_2\text{SO}_4$  required to react with following mixture  
 $\text{NaOH}$  (1mol) +  $\text{Ca}(\text{OH})_2$  (2 mol)
- Q.10 A solution containing 4.2 g of KOH and  $\text{Ca}(\text{OH})_2$  is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample.
- Q.11 How many ml of 0.1 N HCl are required to react completely with 19 gm mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  containing equimolar amounts of two?
- Q.12  $\text{H}_3\text{PO}_4$  is a tri basic acid and one of its salt is  $\text{NaH}_2\text{PO}_4$ . What volume of 1 M NaOH solution should be added to 12 g of  $\text{NaH}_2\text{PO}_4$  to convert it into  $\text{Na}_3\text{PO}_4$ ?

**Redox Titration**

- Q.13 It requires 40 ml of 1M  $\text{Ce}^{4+}$  to titrate 20ml of 1M  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ . What is the oxidation state of the cerium in the product.
- Q.14 A volume of 10.0 ml of 1 M  $\text{SeO}_2$  reacted with exactly 20 ml of 2 M  $\text{CrSO}_4$ . In the reaction,  $\text{Cr}^{2+}$  was oxidized to  $\text{Cr}^{3+}$ . To what oxidation state was selenium converted by the reaction.
- Q.15 Potassium acid oxalate  $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  can be oxidized by  $\text{MnO}_4^-$  in acid medium. Calculate the volume of 0.1M  $\text{KMnO}_4$  reacting in acid solution with 5.08 gm of the acid oxalate.
- Q.16 A 1 g sample of  $\text{H}_2\text{O}_2$  solution containing  $x\%$   $\text{H}_2\text{O}_2$  by mass requires  $x \text{ cm}^3$  of a  $\text{KMnO}_4$  solution for complete oxidation under acidic conditions. Calculate the normality of  $\text{KMnO}_4$  solution.
- Q.17 Metallic tin in the presence of HCl is oxidized by  $\text{K}_2\text{Cr}_2\text{O}_7$  to stannic chloride,  $\text{SnCl}_4$ . What volume of deci-normal dichromate solution would be reduced by 11.9 gm of tin. [Sn = 119]
- Q.18 Calculate the number of millimoles of  $\text{K}_2\text{Cr}_2\text{O}_7$  which will completely react with 40 ml 0.1 M KI solution.
- Q.19 Calculate volume of 0.4 M  $\text{KMnO}_4$  required to react with following in acidic medium.  
 $\text{KHC}_2\text{O}_4$  (1 mol) +  $\text{H}_2\text{C}_2\text{O}_4$  (2 mol)
- Q.20 Calculate volume of 0.4 M NaOH required to react with following mixture.  
 $\text{KHC}_2\text{O}_4$  (1 mol) +  $\text{H}_2\text{C}_2\text{O}_4$  (2 mol)

- Q.21 Calculate volume of 0.2 M  $\text{KMnO}_4$  required to react with following mixture in acidic medium.  
 $\text{KHC}_2\text{O}_4$  (128 gm) +  $\text{H}_2\text{C}_2\text{O}_4$  (180 gm)
- Q.22 520 gm mixture of  $\text{Fe}_2\text{O}_3$  &  $\text{FeO}$  reacts completely with 158 gm  $\text{KMnO}_4$  in acidic medium. Calculate the mole % of  $\text{Fe}_2\text{O}_3$  in mixture.
- Q.23 Calculate the millimoles of  $\text{Br}_2$  produced when 10 ml of 0.1 M  $\text{BrO}_3^-$  reacts with excess of  $\text{Br}^-$ .
- Q.24 5g sample of brass was dissolved in one litre dil.  $\text{H}_2\text{SO}_4$ . 20 ml of this solution were mixed with KI, liberating  $\text{I}_2$  and  $\text{Cu}^+$  and the  $\text{I}_2$  required 20 ml of 0.03 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.
- Q.25 A 0.96 g sample of  $\text{Fe}_2\text{O}_3$  solid of 50% purity is dissolved in acid and completely reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 30 mL of 0.01 M solution of an oxidising agent for titration. Calculate the number of moles of electrons taken up by 1 mol of oxidising agent in the reaction of the above titration.
- Q.26 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the normality of dichromatic solution.
- Q.27 5g of pyrolusite (impure  $\text{MnO}_2$ ) were heated with conc. HCl and  $\text{Cl}_2$  evolved was passed through excess of KI solution. The iodine liberated required 40 mL of  $\frac{N}{10}$  hypo solution. Find the % of  $\text{MnO}_2$  in the pyrolusite.
- Q.28 A 5.0  $\text{cm}^3$  solution of  $\text{H}_2\text{O}_2$  liberates 0.508g of iodine from an acidified KI solution. Calculate the strength of  $\text{H}_2\text{O}_2$  solution in terms of volume strength at STP.
- Q.29 One litre of a mixture of  $\text{O}_2$  and  $\text{O}_3$  ( $\text{O}_3 \longrightarrow \text{O}_2 + \text{O}^{2-}$ ) at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the percent of ozone in the mixture?  
**Assume  $\text{O}_2$  is not interfering in the above reactions.**
- Q.30 An aqueous solution containing 0.10g  $\text{KIO}_3$  (formula wt. = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated  $\text{I}_2$  consumed 45.0 ml of thiosulphate solution to decolourise the blue starch - iodine complex. Calculate the molarity of the sodium thiosulphate solution.
- Q.31 0.56 g of lime stone was treated with oxalic acid to give  $\text{CaC}_2\text{O}_4$ . The precipitate decolorized 45 mL of 0.2N  $\text{KMnO}_4$  in acid medium. Calculate % of CaO in lime stone.
- Q.32 Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of  $\text{KMnO}_4$  (20 mL) acidified with dilute  $\text{H}_2\text{SO}_4$ . The same volume of the  $\text{KMnO}_4$  solution is just decolorized by 10mL of  $\text{MnSO}_4$  in neutral medium simultaneously forming a dark brown precipitate of hydrated  $\text{MnO}_2$ . The brown precipitate is dissolved in 10mL of 0.2M sodium oxalate under boiling condition in the presence of dilute  $\text{H}_2\text{SO}_4$ . Write the balanced equations involved in the reactions and calculate the molarity of  $\text{H}_2\text{O}_2$ .

Back Titration

- Q.33 50gm of a sample of  $\text{Ca(OH)}_2$  is dissolved in 50ml of 0.5N HCl solution. The excess of HCl was titrated with 0.3N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of  $\text{Ca(OH)}_2$ .
- Q.34 One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250ml. To 50ml of this made up solution, 50ml of 0.1N – HCl is added and the mix after shaking well required 10ml of 0.16N – NaOH solution for complete titration. Calculate the % purity of the sample.
- Q.35 10 g  $\text{CaCO}_3$  were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl.
- Q.36 A 3.00g sample containing  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and an inert impure substance, is treated with excess of KI solution in presence of dilute  $\text{H}_2\text{SO}_4$ . The entire iron is converted into  $\text{Fe}^{2+}$  along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the diluted solution require 11.0 ml of 0.5 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution to reduce the iodine present. A 50 ml of the diluted solution, after complete extraction of the iodine requires 12.80 ml of 0.25 M  $\text{KMnO}_4$  solution in dilute  $\text{H}_2\text{SO}_4$  medium for the oxidation of  $\text{Fe}^{2+}$ . Calculate the percentages of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in the original sample.

Double titration

- Q.37 A solution contains  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ , 20ml of this solution required 4ml of 1N HCl for titration with Ph indicator. The titration was repeated with the same volume of the solution but with MeOH. 10.5 ml of 1 N HCl was required this time. Calculate the amount of  $\text{Na}_2\text{CO}_3$  &  $\text{NaHCO}_3$ .
- Q.38 A solution contains a mix of  $\text{Na}_2\text{CO}_3$  and NaOH. Using Ph as indicator 25ml of mix required 19.5 ml of 1 N HCl for the end point. With MeOH, 25 ml of the solution required 25ml of the same HCl for the end point. Calculate g/L of each substance in the mix .
- Q.39 200ml of a solution of mixture of NaOH and  $\text{Na}_2\text{CO}_3$  was first titrated with  $\frac{N}{10}$  HCl with indicator Ph. 17.5 ml of HCl was required for end point. After this MeOH was added and 2.5 ml of same HCl was again required for next end point. Find out amounts of NaOH and  $\text{Na}_2\text{CO}_3$  in the mix.

Hardness of water

- Q.40 Calculate the weight of CaO required to remove hardness of  $10^6$  L of water containing 1.62 gram  $\text{Ca(HCO}_3)_2$  per litre.
- Q.41 Hardness of water is 180 ppm of  $\text{MgSO}_4$ . Express it in terms of ppm of  $\text{CaCO}_3$ .
- Q.42 0.00012 %  $\text{MgSO}_4$  and 0.000111%  $\text{CaCl}_2$  is present in water. What is the measured hardness of water & millimoles of washing soda required to purify 1000 L water.
- Q.43 A sample of hard water contains 96 ppm of  $\text{SO}_4^{2-}$  and 183 ppm of  $\text{HCO}_3^-$ , with  $\text{Ca}^{2+}$  as the only cation. How many moles of CaO will be required to remove  $\text{HCO}_3^-$  from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculate above, what will be the concentration (in ppm) of residual  $\text{Ca}^{2+}$  ions (Assume  $\text{CaCO}_3$  to be completely insoluble in water)?



## EXERCISE-2 (Objective Questions)

Single correct

- $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2$ , then equivalent weight of  $\text{Cr}_2\text{O}_7^{2-}$  is :  
 (A)  $\frac{M}{3}$  (B)  $\frac{M}{6}$  (C)  $\frac{M}{2}$  (D) none
- For the redox reaction,  $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$   
 The correct coefficients of the reactants for the balanced reaction are :  

|     |                  |                             |              |
|-----|------------------|-----------------------------|--------------|
|     | $\text{MnO}_4^-$ | $\text{C}_2\text{O}_4^{2-}$ | $\text{H}^+$ |
| (A) | 2                | 5                           | 16           |
| (B) | 16               | 5                           | 2            |
| (C) | 5                | 16                          | 2            |
| (D) | 2                | 16                          | 5            |
- Which of the following is a redox-reaction-  
 (A)  $2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}$   
 (B)  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$   
 (C)  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3$   
 (D)  $\text{AgNO}_3 + \text{KI} \longrightarrow \text{AgI} + \text{KNO}_3$
- The number of moles of  $\text{KMnO}_4$  that will be needed to react completely with one mole of ferrous oxalate in acid solution is  
 (A)  $3/5$  (B)  $2/5$  (C)  $4/5$  (D) 1
- $\text{MnO}_4^-$  is good oxidising agent in different medium changing to –  

|                                                 |
|-------------------------------------------------|
| $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$ |
| $\longrightarrow \text{MnO}_4^{2-}$             |
| $\longrightarrow \text{MnO}_2$                  |
| $\longrightarrow \text{Mn}_2\text{O}_3$         |

 Changes in oxidation number respectively are –  
 (A) 1, 3, 4, 5 (B) 5, 4, 3, 2 (C) 5, 1, 3, 4 (D) 2, 6, 4, 3
- The normalities of 1 M solution of  $\text{HCl}$ , 1 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{H}_3\text{PO}_4$  in complete neutralization are respectively  
 (A) 1 N, 2 N and 3 N (B) 2 N, 3 N and 1 N  
 (C) 0.1 N, 0.2 N and 0.3 N (D) 3 N, 2 N and 1 N
- An aqueous solution of 6.3 gm of oxalic acid dihydrate is made upto 250 ml. The volume of 0.1 N  $\text{NaOH}$  required to completely neutralize 10 ml of this solution is  
 (A) 40 ml (B) 20 ml (C) 10 ml (D) 4 ml
- In the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  by iodometry the equivalent mass of  $\text{K}_2\text{Cr}_2\text{O}_7$  is  
 (A)  $\frac{\text{M. Mass}}{2}$  (B)  $\frac{\text{M. Mass}}{6}$  (C)  $\frac{\text{M. Mass}}{3}$  (D) Same as M. Mass.

9. If  $m_A$  gram of a metal A displaces  $m_B$  gram of another metal B from its salt solution and if the equivalent weights are  $E_A$  and  $E_B$  respectively then equivalent weight of A can be expressed as
- (A)  $E_A = \frac{m_A}{m_B} \times E_B$  (B)  $E_A = \frac{m_A \times m_B}{E_B}$  (C)  $E_A = \frac{m_B}{m_A} \times E_B$  (D)  $E_A = \sqrt{\frac{m_A}{m_B} \times E_B}$
10. When  $\text{BrO}_3^-$  ion reacts with  $\text{Br}^-$  in acid medium,  $\text{Br}_2$  is liberated. The equivalent weight of  $\text{Br}_2$  in this reaction is
- (A)  $\frac{5M}{8}$  (B)  $\frac{5M}{3}$  (C)  $\frac{3M}{5}$  (D)  $\frac{4M}{6}$
11. 100 ml of  $\text{H}_2\text{O}_2$  is oxidised by 200 ml of 0.01 M  $\text{KMnO}_4$  in acidic medium. 100 ml of same  $\text{H}_2\text{O}_2$  is oxidised by V ml of 0.01 M  $\text{KMnO}_4$  in basic medium ( $\text{MnO}_4^-$  reduced to  $\text{MnO}_2$ .) Hence V is :
- (A) 500 (B) 100 (C)  $\frac{1000}{3}$  (D)  $\frac{500}{3}$
12. In the mixture of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ , volume of a given HCl required is x ml with phenolphthalein indicator and further y ml required with methyl orange indicator. Hence volume of HCl for complete reaction of  $\text{NaHCO}_3$  is :
- (A) 2x (B) y (C)  $\frac{x}{2}$  (D) (y - x)
13. 3.92 g of ferrous ammonium sulphate (Eq. mass = 392) are dissolved in 100 ml of water. 20 ml of this solution requires 200 ml of potassium permanganate during titration for complete oxidation. The weight of  $\text{KMnO}_4$  (Eq. mass = 31.6) present in one litre of the solution is
- (A) 13.6 g (B) 0.316 g (C) 14.76 g (D) 34.78 g
14. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. The equivalent weight of the metal is
- (A) 3.325 (B) 13.25 (C) 23.52 (D) 33.25
15. 0.3gm of a sample of an oxalate salt is dissolved in 100 cc of water. It required 90 cc of N/20  $\text{KMnO}_4$  solution for complete oxidation. The percentage of oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) in the given sample is
- (A) 33 (B) 66 (C) 26 (D) 96
16. What volume of 0.955 M HCl, in milliliters, is needed to titrate 2.152 g of  $\text{Na}_2\text{CO}_3$  to the equivalence point?
- $$\text{Na}_2\text{CO}_3(\text{aq}) + 2\text{HCl}(\text{aq}) \longrightarrow 2\text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$
- (A) 4.25 ml (B) 21.5 ml (C) 84.0 ml (D) 42.5 ml
17. 0.7 g of a sample of  $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$  were dissolved in water and the volume was made to 100 ml. 20 ml of this solution required 19.8 ml of N/10 HCl for complete neutralization. The value of 'x' is:
- (A) 3 (B) 2 (C) 4 (D) 6

18. The ratio of equivalent weights of  $C_2H_5OH$  in the following reactions is :  
 (i)  $C_2H_5OH \longrightarrow CH_3CHO$   
 (ii)  $C_2H_5OH \longrightarrow C_2H_5ONa$   
 (A) 1 : 4 (B) 1 : 1 (C) 1 : 2 (D) 1 : 3
19. An element A in a compound ABD has oxidation number  $A^n$ . It is oxidised by  $Cr_2O_7^{2-}$  in acid medium. In the experiment  $1.68 \times 10^{-3}$  moles of  $K_2Cr_2O_7$  were used for  $3.26 \times 10^{-3}$  moles of ABD. The new oxidation number of A after oxidation is :  
 (A) 3 (B)  $3 - n$  (C)  $n - 3$  (D)  $+n$
20. When the ion  $Cr_2O_7^{2-}$  acts as an oxidant in acidic aqueous solution the ion  $Cr^{3+}$  is formed. How many mole of  $Sn^{2+}$  would be oxidised to  $Sn^{4+}$  by one mole  $Cr_2O_7^{2-}$  ion :  
 (A) 2/3 (B) 3/2 (C) 2 (D) 3
21. A sample of hard water contain 20 mg of  $Ca^{2+}$  ions per litre. How many milli equivalent of  $Na_2CO_3$  would be required to soften 1 litre of the sample?  
 (A) 0.5 (B) 0.1 (C) 0.2 (D) 1
22. 1 litre solution of unknown molarity is titrated by taking its 50 mL solution against KI solution in strong acid medium of excess HCl. The equivalence point was detected when 10 mL of 0.1 M KI was consumed. The molarity of  $KIO_3$  solution is :  
 (A)  $4 \times 10^{-4}$  M (B)  $2 \times 10^{-2}$  M (C)  $4 \times 10^{-3}$  M (D)  $2 \times 10^{-3}$  M
23.  $BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$   
 If 25.0 mL of 0.200 molar  $BrO_3^-$  is mixed with 30.0 mL of 0.450 molar  $Br^-$  solution that contains a large excess of  $H^+$ , the amount of  $Br_2$  formed, according to the equation above, is  
 (A)  $5.00 \times 10^{-3}$  mole (B)  $8.10 \times 10^{-3}$  mole  
 (C)  $1.35 \times 10^{-2}$  mole (D)  $1.50 \times 10^{-2}$  mole
24. An equimolar mixture of  $Na_2C_2O_4$  and  $H_2C_2O_4$  required  $V_1$  litre of 0.1 M  $KMnO_4$  in acidic medium for complete oxidation. The same amount of the mixture required  $V_2$  litre of 0.2 M NaOH for neutralization. The ratio of  $V_1$  to  $V_2$  ( $V_1/V_2$ ) is :  
 (A) 2 : 5 (B) 1 : 2 (C) 4 : 5 (D) None of these
25. 1 gram of a sample of  $CaCO_3$  was strongly heated and the  $CO_2$  liberated was absorbed in 100 mL of 0.5 M NaOH. Assuming 90% purity for the sample. How much mL of 0.5 M HCl would be required to react with the solution of the alkali to reach the phenolphthalein end point?  
 (A) 73 mL (B) 41 mL (C) 82 mL (D) 87 mL

One or more correct

26. Which of the following represent redox reactions :  
 (A)  $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$  (B)  $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$   
 (C)  $2\text{MnO}_4^- + 3\text{Mn}^{2+} \longrightarrow 5\text{MnO}_2$  (D)  $2\text{Cu}^+ \longrightarrow \text{Cu} + \text{Cu}^{2+}$
27. For the reaction :  
 $\text{H}_3\text{PO}_4 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaHPO}_4 + 2\text{H}_2\text{O}$   
 1 mol      1 mol  
 which are true statements :  
 (A) equivalent weight of  $\text{H}_3\text{PO}_4$  is 49 (B) resulting mixture is neutralised by 1 mol of KOH.  
 (C)  $\text{CaHPO}_4$  is an acid salt  
 (D) 2 mol of  $\text{H}_3\text{PO}_4$  is completely neutralised by 1.5 mol of  $\text{Ca}(\text{OH})_2$ .
28. 11.2 g of mixture of MCl (volatile) and NaCl gave 28.7 g of white ppt with excess of  $\text{AgNO}_3$  solution. 11.2 g of same mixture on heating gave a gas that on passing into  $\text{AgNO}_3$  solution gave 14.35 g of white ppt. Hence :  
 (A) ionic mass of  $\text{M}^+$  is 18 (B) mixture has equal mol fraction of MCl and NaCl  
 (C) MCl and NaCl are in 1 : 2 molar ratio (D) atomic mass of M is 10
29.  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  behave as acids as well as reducing agents. Which are correct statements ?  
 (A) equivalent weight of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  are equal to their molecular weights when behaving as reducing agents  
 (B) 100 ml of 1 N solution of each is neutralised by equal volume of 1 M  $\text{Ca}(\text{OH})_2$   
 (C) 100 ml of 1 N solution of each is neutralised by equal volumes of 1 N  $\text{Ca}(\text{OH})_2$   
 (D) 100 ml of 1 M solution of each is oxidised by equal volumes of 1 M  $\text{KMnO}_4$
30. A solution of  $\text{Na}_2\text{S}_2\text{O}_3$  is iodometrically titrated against 0.25050 g of  $\text{KBrO}_3$ . This process requires 90 ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution the strength of the  $\text{Na}_2\text{S}_2\text{O}_3$  is [ $\text{BrO}_3^-$  reduces into  $\text{Br}^-$ ]  
 (A) 0.2 M (B) 0.1 M (C) 0.05 M (D) 0.1 N
31. Consider the following redox reaction :  
 $\text{KMnO}_4 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{K}^+$   
 Which of the following is (are) true regarding the above redox reaction?  
 (A)  $\frac{5}{8}$  mol of  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidized by one mole of  $\text{KMnO}_4$ .  
 (B) Oxidation number of sulphur changes from +4 to +12.  
 (C) Change of medium from acidic to basic will have no effect on the stoichiometry of reaction.  
 (D) Change in medium from acidic to basic will change the nature of product.
32. A sample of steel weighing 0.30 g was subjected to a chemical reaction to convert its sulphur impurity to  $\text{H}_2\text{S}(\text{g})$ . The evolved gas required 2.40 mL 0.02 N iodine solution. Which of the following statement(s) is (are) true?  
 (A) Iodine is reduced to iodide (B)  $\text{H}_2\text{S}$  is oxidized to S  
 (C) Steel contain 0.256% of S by weight  
 (D) The reaction of  $\text{H}_2\text{S}$  with  $\text{I}_2$  is a precipitation reaction rather than a redox reaction

Match the column :

33. Match List I (compounds) with List II (oxidation state of nitrogen) and select the correct answer using the codes given below the lists :

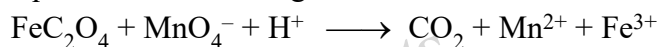
**List I**

- (A)  $\text{NaN}_3$   
(B)  $\text{N}_2\text{H}_4$   
(C)  $\text{NO}$   
(D)  $\text{N}_2\text{O}_5$

**List II**

- (P) +5  
(Q) +2  
(R)  $-\frac{1}{3}$   
(S) -2

34. Match the stoichiometric coefficients in List I with the species in List II and involved in the balanced equation of the following reaction:



**List I**

- (A)  $\text{FeC}_2\text{O}_4$   
(B)  $\text{MnO}_4^-$   
(C)  $\text{H}^+$   
(D)  $\text{CO}_2$

**List II**

- (P) 3  
(Q) 5  
(R) 10  
(S) 24

35. Match the following

**List I**

- (A) Change of  $\text{NO}$  to  $\text{NO}_3^-$   
(B) Change of  $\text{P}_4$  to  $\text{H}_2\text{PO}_2^-$   
(C)  $\text{KMnO}_4$  in acidic medium  
(D)  $\text{K}_2\text{Cr}_2\text{O}_7$  in acidic medium

**List II**

- (P) Oxidation number changes from +7 to +2  
(Q) Oxidation number changes +6 to +3  
(R) Oxidation number changes from 0 to +1  
(S) Oxidation number changes from +2 to +5.

36. Consider the redox-reactions of Column I and match them with the entries of with Column II.

**Column I**

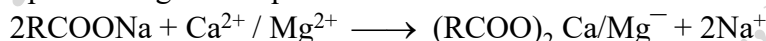
- (A)  $\text{KMnO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{2+} + \text{O}_2$   
(B)  $\text{K}_2\text{CrO}_4 + \text{H}_2\text{S} \rightarrow \text{Cr}^{3+} + \text{SO}_2$   
(C)  $\text{H}_2\text{O}_2 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{H}_2\text{O} + \text{CO}_2$   
(D)  $\text{K}_2\text{CrO}_4 + \text{FeS} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + \text{SO}_2$

**Column II**

- (P) One mole of reducing agent reduces more than two moles of oxidizing agent.  
(Q) One mole of oxidizing agent oxidizes more than one mole of reducing agent.  
(R) One mole of oxidizing agent oxidizes less than one mole of reducing agent.  
(S) One mole of oxidizing agent oxidizes one mole of reducing agent.

**Question No. 37 to 39 (3 questions)**

Hard water is having soluble salts of calcium and magnesium which forms precipitates with the carboxylate ion present in soap according to the equation.



On the basis of removal of hardness, it can be of two types :

- (1) Temporary hardness and (2) Permanent hardness

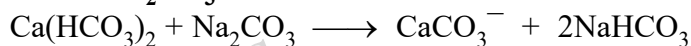
- (1) **Temporary hardness** : It is due the presence of bicarbonates of calcium and magnesium in water.

It is easily removed by following processes :

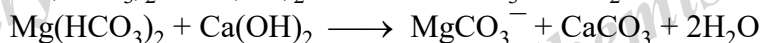
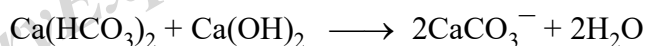
(a) **By boiling of water**



(b) By the addition of  $\text{Na}_2\text{CO}_3$



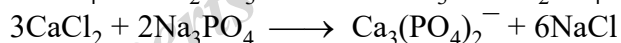
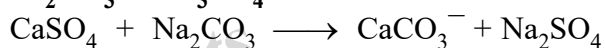
(c) **Clarke's process** : By the addition of exact amount of  $\text{Ca}(\text{OH})_2$ , because excess will also impart hardness in water.



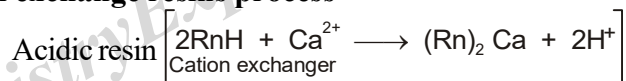
- (2) **Permanent hardness** : It is due the present of chlorides and sulphates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . It can not be removed by boiling or by the addition of  $\text{Ca}(\text{OH})_2$ .

**Removal of permanent hardness**

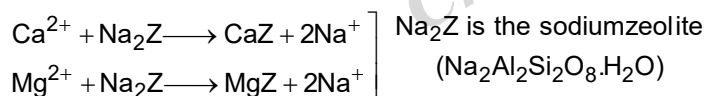
(i) By adding  $\text{Na}_2\text{CO}_3$  or  $\text{Na}_3\text{PO}_4$



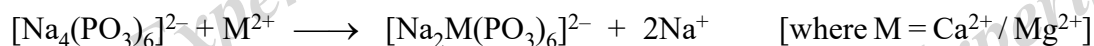
(ii) **Ion exchange resins process**



(iii) **Permutit process**



(iv) **Calgon (calcium gone) process** :  $\text{Na}_6(\text{PO}_3)_6$  is called calgon which is written as  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$



37. One litre of a sample of hard water contains 1 mg of  $\text{CaCl}_2$  and 1 mg of  $\text{MgCl}_2$ . Then the total hardness in terms of parts of  $\text{CaCO}_3$  per  $10^6$  parts of water by mass is :  
 (A) 1.954 ppm (B) 1.260 (C) 0.946 (D) None of these
38. Consider the temporary hardness of water is due to the presence of  $\text{Ca}(\text{HCO}_3)_2$  and specific gravity of hard water is 1. Then the weight of  $\text{CaO}$  required for  $10^6$  litre of water remove the temporary hardness of 1000 ppm is:  
 (A)  $3.6 \times 10^4$  gm (B)  $6.5 \times 10^4$  gm (C)  $5.6 \times 10^5$  gm (D)  $8.5 \times 10^5$  gm
39. For a given sample of water containing the following impurities.  
 $\text{Mg}(\text{HCO}_3)_2 = 73$  mg/L.  $\text{Ca}(\text{HCO}_3)_2 = 162$  mg/L.  $\text{CaSO}_4 = 136$  mg/L.  
 $\text{MgCl}_2 = 95$  mg/L.  $\text{CaCl}_2 = 111$  mg/L and  $\text{NaCl} = 100$  mg/L  
 Then the total hardness (temporary and permanent) of above water sample is :  
 (A) 300 ppm (B) 350 ppm (C) 450 ppm (D) 500 ppm

**Assertion & Reason :**

**40. Statement-1** In  $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$ ,  $\text{MnO}_4^-$  acts as oxidizing agent and  $\text{Fe}^{2+}$  acts as reducing agent.

**Statement-2** The reactions involving simultaneous loss or gain of electron among the reacting species are called oxidation-reduction reactions.

(A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1

(B) Statement-1 is true, Statement-2 is true and Statement-2 is **NOT** correct explanation for Statement-1

(C) Statement-1 is true, Statement-2 is false

(D) Statement-1 is false, Statement-2 is true

**41. Statement-1** In the balanced redox reaction  $x\text{Cu}_2\text{O} + y\text{NO}_3^- + 14\text{H}^+ \longrightarrow 6\text{Cu}^{2+} + \text{NO} + 7\text{H}_2\text{O}$ , the n-factor of  $\text{Cu}_2\text{O}$  and  $\text{NO}_3^-$  is 2 and 3 respectively.

**Statement-2** Since reciprocal of n-factor's ratio is molar ratio and so,  $x : y = 2 : 3$

(A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1

(B) Statement-1 is true, Statement-2 is true and Statement-2 is **NOT** correct explanation for Statement-1

(C) Statement-1 is true, Statement-2 is false

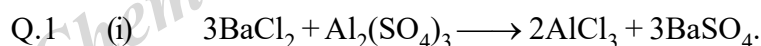
(D) Statement-1 is false, Statement-2 is true

# ANSWER KEY

## EXERCISE-ZERO

- Q.1 (1) -1 (2) +2 (3) +1 (4) -3 (5) +4 (6) +5  
 (7) +6 (8) -3 (9) -3 (10) -1/3 (11) +2 (12) +1  
 (13) +5 (14) +2 (15) +7 (16) +6 (17) +3 (18) +6  
 (19) +6 (20) +2

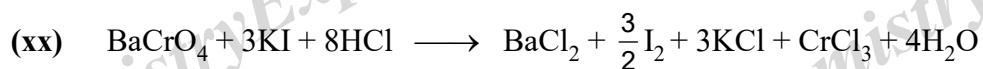
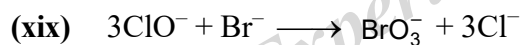
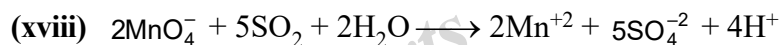
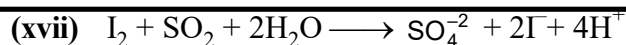
- Q.2 (1)  $+\frac{8}{3}$  (2) +1 (3) +2.5 (4) -2 (5) +2 (6) +1  
 (7) +2 (8) zero (9) +1 (10) +6 (11) -3 (12) +6  
 (13) +2 (14) +2 (15) +1 (16) +8 (17) -1 (18) +6  
 (19) +8 (20) +4 (21) +3 (22) +5 (23) +6 (24) +8/3  
 (25) +3 (26) +6 (27) +200/93



## EXERCISE-1

- Q.1 (i)  $4\text{Zn} + \text{NO}_3^- + 10\text{H}^+ \longrightarrow 4\text{Zn}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$   
 (ii)  $\text{I}_2 + 10\text{NO}_3^- + 8\text{H}^+ \longrightarrow 2\text{IO}_3^- + 10\text{NO}_2 + 4\text{H}_2\text{O}$   
 (iii)  $\text{H}_2\text{O}_2 + 2\text{ClO}_2 + 2[\text{OH}]^- \longrightarrow 2\text{ClO}_2^- + \text{O}_2 + 2\text{H}_2\text{O}$   
 (iv)  $3\text{Cl}_2 + 6\text{KOH} \longrightarrow \text{KClO}_3 + 5\text{KCl} + 3\text{H}_2\text{O}$   
 (v)  $3\text{H}_2\text{O}_2 + 2\text{KMnO}_4 \longrightarrow 2\text{MnO}_2 + 2\text{KOH} + 3\text{O}_2 + 2\text{H}_2\text{O}$   
 (vi)  $5\text{HNO}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow 5\text{HNO}_3 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$   
 (vii)  $\text{NaNO}_2 + \text{NaI} + \text{H}_2\text{SO}_4 \longrightarrow \text{NO} + \frac{1}{2} \text{I}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$   
 (viii)  $3\text{P} + 5\text{HNO}_3 \longrightarrow 3\text{HPO}_3 + 5\text{NO} + \text{H}_2\text{O}$   
 (ix)  $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \longrightarrow 2\text{KCl} + 2\text{CrCl}_3 + 7\text{H}_2\text{O} + 3\text{Cl}_2$   
 (x)  $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow 10\text{CO}_2 + 2\text{Mn}^{+2} + 8\text{H}_2\text{O}$   
 (xi)  $\text{Cr}_2\text{O}_7^{2-} + 3\text{C}_2\text{O}_4^{2-} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 6\text{CO}_2 + 7\text{H}_2\text{O}$   
 (xii)  $2\text{KMnO}_4 + 5\text{H}_2\text{S} + 4\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + 2\text{MnSO}_4 + 5\text{S} + 8\text{H}_2\text{O}$   
 (xiii)  $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{I}_2 + 2\text{H}_2\text{O}$   
 (xiv)  $\text{Cr}_2\text{O}_7^{2-} + 3\text{NO}_2^- + 8\text{H}^+ \longrightarrow 2\text{Cr}^{+3} + 3\text{NO}_3^- + 4\text{H}_2\text{O}$   
 (xv)  $3\text{AsO}_3^{3-} + \text{IO}_3^- \longrightarrow 3\text{AsO}_4^{3-} + \text{I}^-$   
 (xvi)  $3\text{H}_2\text{S} + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \longrightarrow 2\text{Cr}^{+3} + \frac{3}{8}\text{S}_8 + 7\text{H}_2\text{O}$





Q.2 (i) 2 (ii) 2 (iii) 5 (iv) 1 (v) 2 (vi) 1 (vii) 2 (viii) 1

Q.3 (i) 1 (ii) 2 (iii) 1 (iv) 2 (v) 3 (vi) 1 (vii) 2 (viii) 1 (ix) 2

Q.4 (a) 4/3 (b) 2 (c) 8 (d) 7/4 (e) 28, 2 (f) 10 (g) 12 (h) 13/3 (i) 61

Q.5 1 Q.6 40ml Q.7 60ml Q.8 12.5 l

Q.9 12.5 l

Q.10  $\text{KOH} = 35\%$ ,  $\text{Ca(OH)}_2 = 65\%$  Q.11  $V = 3$  lit.

Q.12 200 mL Q.13 + 3 Q.14 zero Q.15  $V = 160$  ml

Q.16 0.588 N Q.17 4 lit. Q.18  $\frac{2}{3}$  Q.19 3 l

Q.20 12.5 l Q.21 6 l Q.22 16.66% Q.23 3

Q.24 38 % Q.25 5 Q.26 0.15 N Q.27 0.174g; 3.48%

Q.28 4.48% Q.29 6.57%  $\text{O}_3$  (by weight) Q.30 0.0623M

Q.31 45% Q.32 0.1M Q.33 1.406% Q.34 90.1%

Q.35  $V = 25$  mL Q.36  $\text{Fe}_2\text{O}_3 = 49.33\%$ ,  $\text{Fe}_3\text{O}_4 = 34.8\%$  Q.37 0.424 gm ; 0.21 gm

Q.38 23.32 gm ; 22.4 gm Q.39 0.06 gm ; 0.265 gm Q.40 560 Kg

Q.41 150 ppm Q.42 2 ppm, 20 m mole. Q.43 1.5, 40 ppm

### EXERCISE-2

1. B 2. A 3. A 4. A 5. C 6. A 7. A

8. B 9. A 10. C 11. C 12. D 13. B 14. D

15. B 16. D 17. B 18. C 19. B 20. D 21. D

22. C 23. B 24. C 25. C

26. CD 27. ABC 28. AB 29. BCD 30. BD 31. AD 32. ABC

33.  $A \rightarrow R$  ;  $B \rightarrow S$  ;  $C \rightarrow Q$  ;  $D \rightarrow P$  34.  $A \rightarrow Q$  ;  $B \rightarrow P$  ;  $C \rightarrow S$  ;  $D \rightarrow R$

35.  $A \rightarrow S$  ;  $B \rightarrow R$  ;  $C \rightarrow P$  ;  $D \rightarrow Q$  36.  $A \rightarrow Q$  ;  $B \rightarrow R$  ;  $C \rightarrow S$  ;  $D \rightarrow P, R$

37. A 38. C 39. C

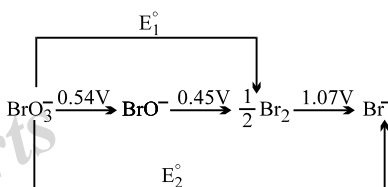
40. B 41. C

## EXERCISE-1 (Subjective Questions)

### GALVANIC CELL

#### Electrode potential and standard electrode potential

- Q.1 For the cell reaction  $2\text{Ce}^{4+} + \text{Co} \longrightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$   
 $E^\circ_{\text{cell}}$  is 1.89 V. If  $E^\circ_{\text{Co}^{2+}|\text{Co}}$  is  $-0.28$  V, what is the value of  $E^\circ_{\text{Ce}^{4+}|\text{Ce}^{3+}}$ ?
- Q.2 Determine the standard reduction potential for the half reaction:  $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$   
 Given  $\text{Pt}^{2+} + 2\text{Cl}^- \longrightarrow \text{Pt} + \text{Cl}_2$ ,  $E^\circ_{\text{cell}} = -0.15$  V  
 $\text{Pt}^{2+} + 2\text{e}^- \longrightarrow \text{Pt}$ ,  $E^\circ = 1.20$  V
- Q.3 Is 1.0 M  $\text{H}^+$  solution under  $\text{H}_2\text{SO}_4$  at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M  $\text{Ag}^+$  ion?  
 $E^\circ_{\text{Ag}^+|\text{Ag}} = 0.80$  V,  $E^\circ_{\text{H}^+|\text{H}_2(\text{Pt})} = 0.0$  V
- Q.4 If for the half cell reactions:  
 $\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$  ;  $E^\circ = 0.15$  V  
 $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$  ;  $E^\circ = 0.34$  V  
 Calculate  $E^\circ$  of the half cell reaction  $\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$   
 Also predict whether  $\text{Cu}^+$  undergoes disproportionation or not.
- Q.5 If  $E^\circ_{\text{Fe}^{2+}|\text{Fe}} = -0.44$  V,  $E^\circ_{\text{Fe}^{3+}|\text{Fe}^{2+}} = 0.76$  V. Calculate  $E^\circ_{\text{Fe}^{3+}|\text{Fe}}$ .
- Q.6 Consider the following  $E^\circ$  values  
 $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.76$  V  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44$  V  $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14$  V  
 Under standard conditions, calculate the EMF for the cell reaction.  
 $3\text{Sn}_{(\text{s})} + 2\text{Fe}^{3+}(\text{aq}) \longrightarrow 2\text{Fe}(\text{aq}) + 3\text{Sn}^{2+}(\text{aq})$
- Q.7 From the standard potentials shown in the following diagram, calculate the potentials  $E_1^\circ$  and  $E_2^\circ$ .

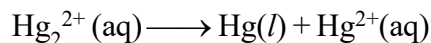


- Q.8 Calculate the equilibrium constant for the reaction  
 $\text{Fe}^{2+} + \text{Ce}^{4+} \longrightarrow \text{Fe}^{3+} + \text{Ce}^{3+}$ , [Given :  $E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44$  V;  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68$  V]  
 Take  $\frac{2.303 RT}{F} = 0.06$  at  $25^\circ\text{C}$ ,  $\log 4.68 = 0.67$
- Q.9 Calculate the equilibrium constant for the reaction  $\text{Fe} + \text{CuSO}_4 \longrightarrow \text{FeSO}_4 + \text{Cu}$  at  $25^\circ\text{C}$ .  
 Given :  $E^\circ(\text{Fe}/\text{Fe}^{2+}) = 0.44$  V,  $E^\circ(\text{Cu}/\text{Cu}^{2+}) = -0.337$  V.  
 Take  $\frac{2.303 RT}{F} = 0.06$  at  $25^\circ\text{C}$ ,  $\log 7.94 = 0.9$

- Q.10 At 25°C the value of K for the equilibrium  $\text{Fe}^{3+} + \text{Ag} \longrightarrow \text{Fe}^{2+} + \text{Ag}^+$  is 0.531 mol/litre. The standard electrode potential for  $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$  is 0.8V. What is the standard potential for  $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$ ?

Given :  $\frac{2.303RT}{F} = 0.06, \quad \log (0.531) = -0.275$

- Q.11 Calculate equilibrium constant for :



Given :  $E^\circ_{\text{Hg}_2^{2+}(\text{aq})/\text{Hg}(\text{l})} = 0.8\text{V} \quad E^\circ_{\text{Hg}_2^{2+}(\text{aq})/\text{Hg}^{2+}(\text{aq})} = -0.92\text{V}$

### Nernst Equation

- Q.12 Calculate the EMF of a Daniel cell when the concentration of  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  are 0.001 M and 0.1M respectively. The standard EMF of the cell is 1.1V.

- Q.13 For a cell  $\text{Mg}(\text{s}) | \text{Mg}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$ , calculate the equilibrium constant at 25°C. Also find the maximum work per mole of Mg that can be obtained by operating the cell.  
 $E^\circ(\text{Mg}^{2+}/\text{Mg}) = -2.38\text{V}, E^\circ(\text{Ag}^+/\text{Ag}) = 0.8\text{V}.$

- Q.14 The EMF of the cell  $\text{M} | \text{M}^{n+}(0.01\text{M}) || \text{H}^+(1\text{M}) | \text{H}_2(\text{g})(1\text{ atm}), \text{Pt}$  at 25°C is 0.82V. Calculate the valency of the metal if the standard oxidation potential of the metal is 0.76V.

Take  $\frac{2.303 RT}{F} = 0.06$  at 25°C.

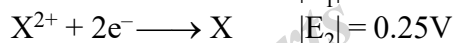
- Q.15 Calculate  $E^\circ$  and E for the cell  $\text{Sn} | \text{Sn}^{2+}(1\text{M}) || \text{Pb}^{2+}(10^{-3}\text{M}) | \text{Pb}$ ,  $E^\circ(\text{Sn}^{2+} | \text{Sn}) = -0.14\text{V}$ ,  $E^\circ(\text{Pb}^{2+} | \text{Pb}) = -0.13\text{V}$ . Is cell representation correct?

- Q.16 At what concentration of  $\text{Cu}^{2+}$  in a solution of  $\text{CuSO}_4$  will the electrode potential be zero at 25°C?

Given :  $E^\circ(\text{Cu} | \text{Cu}^{2+}) = -0.34\text{V}.$

Take  $\frac{2.303 RT}{F} = 0.06$  at 25°C,  $\log 4.68 = 0.67$

- Q.17 The magnitude of standard reduction potentials of two metals 'X' and 'Y' are



When two half cells of X and Y are connected to construct a galvanic cell, electrons flow in the external circuit from X to Y. When X is connected to a standard SHE, electrons flow in the external circuit from X to SHE. If a half cell  $\text{X}^{2+}(0.1\text{M}) | \text{X}$  is connected to another half cell  $\text{Y}^{2+}(1.0\text{M}) | \text{Y}$  to construct a galvanic cell at 25°C, Calculate the EMF of cell :

(Given : At 25°C ;  $\frac{2.303 RT}{F} = 0.06$ )

- Q.18 Two students use same stock solution of  $\text{ZnSO}_4$  and a solution of  $\text{CuSO}_4$ . The e.m.f of one cell is 0.03 V higher than the other. The conc. of  $\text{CuSO}_4$  in the cell with higher e.m.f value is 0.5 M. Find out

the conc. of  $\text{CuSO}_4$  in the other cell  $\left( \frac{2.303 RT}{F} = 0.06 \right)$

- Q.19 If potential of the cell is 0.98 V at 25°C. Then calculate the pH in anodic compartment.  
 $\text{Pt(s)} \mid \text{H}_2(1 \text{ atm}) \mid \text{H}^+(\text{aq}) \parallel \text{Ag}^+(0.1 \text{ M}) \mid \text{Ag(s)}$
- [Given :  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.8 \text{ V}$  and  $\frac{2.303RT}{F} = 0.06$ ]
- Q.20 Voltage of the cell  $\text{Pt, H}_2(1 \text{ atm}) \mid \text{HOCN}(10^{-3} \text{ M}) \parallel \text{Ag}^+(0.8 \text{ M}) \mid \text{Ag(s)}$  is 0.98V . Calculate the  $K_a$  for HOCN . Neglect  $[\text{H}^+]$  because of oxidation of  $\text{H}_2(\text{g})$  .  
 $\text{Ag}^+ + \text{e} \longrightarrow \text{Ag(s)} = 0.8 \text{ V}$ .
- Given :  $\frac{2.303RT}{F} = 0.06$
- Q.21 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1M  $\text{MnO}_4^-$  and 0.5M  $\text{H}^+$  and which was treated with 50% of the  $\text{Fe}^{2+}$  necessary to reduce all the  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ .  
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}, E^0 = 1.51 \text{ V}$
- Given :  $\frac{2.303RT}{F} = 0.06$
- Q.22 A zinc electrode is placed in a 0.1M solution at 25°C. Assuming that the salt is 20% dissociated at this dilution, calculate the electrode potential.  $E^0(\text{Zn}^{2+} \mid \text{Zn}) = -0.76 \text{ V}$ .  $[\log 2 = 0.3]$

## CONCENTRATION CELLS

- Q.23 Calculate the EMF of the following cell at 298 K.  

$$\text{Zn} | \text{Zn}^{2+} (0.01\text{M}) || \text{Zn}^{2+} (0.1\text{M}) | \text{Zn}$$
- Q.24 Equinormal Solutions of two weak acids, HA ( $\text{pK}_a = 3$ ) and HB ( $\text{pK}_a = 5$ ) are each placed in contact with equal pressure of hydrogen electrode at  $25^\circ\text{C}$ . When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.
- Q.25 In two vessels each containing 500ml water, 0.5 millimol of aniline ( $\text{K}_b = 10^{-9}$ ) and 25 m mol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately. ( $\log 5 = 0.7$ )
- Q.26 Calculate pH using the following cell :  

$$\text{Pt} (\text{H}_2) | \text{H}^+ (x\text{M}) || \text{H}^+ (1\text{M}) | \text{Pt} (\text{H}_2) \text{ if } E_{\text{cell}} = 0.2364\text{ V.}$$

$$1\text{ atm} \qquad \qquad \qquad 1\text{ atm}$$
- Q.27 Calculate the emf of the cell  

$$\text{Pt}, \text{H}_2 (1.0\text{ atm}) | \text{HA} (0.1\text{M}) || \text{RNH}_2 (\text{aq}, 0.01\text{M}) | \text{H}_2 (1.0\text{ atm}), \text{Pt}$$

$$\text{K}_a \text{ HA} = 10^{-5}, \text{K}_b \text{ RNH}_2 = 10^{-6}.$$

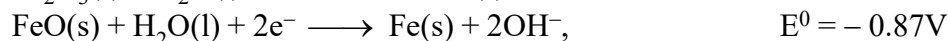
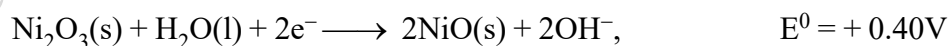
Given :  $\frac{2.303RT}{F} = 0.06$

CELL CONSISTING SPECIAL HALF-CELLS

- Q.28 The standard reduction potential for  $\text{Cu}^{2+} / \text{Cu}$  is 0.34 V. Calculate the reduction potential at  $\text{pH} = 14$  for the  $\text{Pt}, \text{KOH} / \text{Cu}(\text{OH})_2 / \text{Cu}$  couple.  $K_{\text{sp}}$  of  $\text{Cu}(\text{OH})_2$  is  $1 \times 10^{-19}$ .

Given :  $\frac{2.303RT}{F} = 0.06$

- Q.29 The Edison storage cell is represented as  $\text{Fe}(\text{s}) | \text{FeO}(\text{s}) | \text{KOH}(\text{aq}) | \text{Ni}_2\text{O}_3(\text{s}) | \text{NiO}(\text{s})$  The half-cell reaction are



- What is the cell reaction?
- What is the cell e.m.f.? How does it depend on the concentration of  $\text{KOH}$ ?
- What is the maximum amount of electrical energy that can be obtained from one mole of  $\text{Ni}_2\text{O}_3$ ?

- Q.30 Consider the cell  $\text{Ag} | \text{AgBr}(\text{s}) | \text{Br}^- || \text{AgCl}(\text{s}), \text{Ag} | \text{Cl}^-$  at  $25^\circ\text{C}$ . The solubility product constants of  $\text{AgBr}$  &  $\text{AgCl}$  are  $5 \times 10^{-13}$  &  $1 \times 10^{-10}$  respectively. For what ratio of the concentrations of  $\text{Br}^-$  &  $\text{Cl}^-$  ions would the emf of the cell be zero?

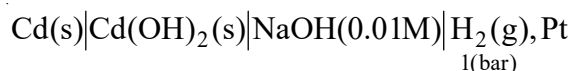
- Q.31 The  $\text{p}K_{\text{sp}}$  of  $\text{AgI}$  is 16.5. If the  $E^0$  value for  $\text{Ag}^+ | \text{Ag}$  is 0.80V. Find the  $E^0$  for the half cell reaction  $\text{AgI}(\text{s}) + \text{e}^- \longrightarrow \text{Ag} + \text{I}^-$ .

Given :  $\frac{2.303RT}{F} = 0.06$

- Q.32  $\text{Ag} | \text{AgBr}(\text{s}), \text{KBr}(0.01\text{M}) || \text{KCl}(0.002\text{M}), \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$   
Calculate the EMF of given cell at  $25^\circ\text{C}$  :

[Given :  $K_{\text{sp}}(\text{AgCl}) = 4.8 \times 10^{-10} \text{ M}^2$ ,  $K_{\text{sp}}(\text{AgBr}) = 2.4 \times 10^{-14} \text{ M}^2$  and  $\frac{2.303RT}{F} = 0.06$ ]

- Q.33 Given the cell



with  $E_{\text{cell}} = 0$ , then, Calculate the  $K_{\text{sp}}$  of  $\text{Cd}(\text{OH})_2$  -

[Given :  $E^0_{\text{Cd}^{+2}/\text{Cd}} = -0.39\text{V}$  and  $\frac{2.303RT}{F} = 0.06$ ]

- Q.34 Calculate the standard reduction potential of  $\text{CuS}/\text{Cu}$  electrode.

[Given  $K_{\text{sp}}$  of  $\text{CuS}$  is  $10^{-36} \text{ M}^2$ ,  $E^0_{\text{Cu}^{+2}/\text{Cu}} = 0.34 \text{ volt}$ ,  $\frac{2.303RT}{F} = 0.06$ ]

- Q.35 For the galvanic cell :  $\text{Ag} | \text{AgCl}(\text{s}) | \text{KCl}(0.2\text{M}) || \text{KBr}(0.001\text{M}) | \text{AgBr}(\text{s}) | \text{Ag}$ ,  
Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at  $25^\circ\text{C}$ . [ $K_{\text{sp}}(\text{AgCl}) = 2.64 \times 10^{-10}$ ;  $K_{\text{sp}}(\text{AgBr}) = 3.3 \times 10^{-13}$ ]

- Q.36 For the cell :  $\text{Pt}/\text{Hg}_{(l)}/\text{Hg}_2\text{Cl}_{2(s)}/\text{Cl}^-(0.1\text{M})\|\text{Cl}^-(0.01\text{M})/\text{Cl}_2(1\text{ atm})/\text{Pt}$   
 $E_{\text{cell}}$  is equal to 1.16V. What will be the value of  $E_{\text{cell}}^\circ$ ?
- Q.37 Given,  $E^\circ = -0.276\text{V}$  for the  $\text{Cl}^-|\text{PbCl}_2|\text{Pb}$  couple and  $-0.126\text{V}$  for the  $\text{Pb}^{2+}|\text{Pb}$  couple, determine  $K_{\text{sp}}$  for  $\text{PbCl}_2$  at  $25^\circ\text{C}$ ? [Given :  $\frac{2.303RT}{F} = 0.06$ ]
- Q.38 Find the solubility product of a saturated solution of  $\text{Ag}_2\text{CrO}_4$  in water at 298 K if the emf of the cell  $\text{Ag}|\text{Ag}^+(\text{satd. Ag}_2\text{CrO}_4\text{ soln.})\|\text{Ag}^+(0.1\text{ M})|\text{Ag}$  is 0.164 V at 298K.
- Q.39 The standard potential of the following cell is 0.23 V at  $15^\circ\text{C}$  & 0.21 V at  $35^\circ\text{C}$   
 $\text{Pt}|\text{H}_2(\text{g})|\text{HCl}(\text{aq})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$   
 (i) Write the cell reaction.  
 (ii) Calculate  $\Delta H^\circ, \Delta S^\circ$  for the cell reaction by assuming that these quantities remain unchanged in the range  $15^\circ\text{C}$  to  $35^\circ\text{C}$ .  
 (iii) Calculate the solubility of  $\text{AgCl}$  in water at  $25^\circ\text{C}$ . Given standard reduction potential of the  $\text{Ag}^+/\text{Ag}$  couple is 0.80 V at  $25^\circ\text{C}$ .
- Q.40 Calculate the equilibrium constant for the reaction:  
 $3\text{Sn}(\text{s}) + 2\text{Cr}_2\text{O}_7^{2-} + 28\text{H}^+ \longrightarrow 3\text{Sn}^{4+} + 4\text{Cr}^{3+} + 14\text{H}_2\text{O}$   
 $E^\circ$  for  $\text{Sn}/\text{Sn}^{2+} = 0.136\text{V}$   $E^\circ$  for  $\text{Sn}^{2+}/\text{Sn}^{4+} = -0.156\text{V}$   
 $E^\circ$  for  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} = 1.35\text{V}$   
 Given :  $\frac{2.303RT}{F} = 0.06$
- Q.41 Calculate the equilibrium constant for the reaction,  $2\text{Fe}^{3+} + 3\text{I}^- \longrightarrow 2\text{Fe}^{2+} + \text{I}_3^-$ . The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{I}_3^-/\text{I}^-$  couples.
- Q.42 For the reaction,  $4\text{Al}(\text{s}) + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O} + 4\text{OH}^- \longrightarrow 4[\text{Al}(\text{OH})_4^-]$ ;  $E_{\text{cell}}^\circ = 2.73\text{V}$ . If  $\Delta G_f^\circ(\text{OH}^-) = -157\text{ kJ mol}^{-1}$  and  $\Delta G_f^\circ(\text{H}_2\text{O}) = -237.2\text{ kJ mol}^{-1}$ , determine  $\Delta G_f^\circ[\text{Al}(\text{OH})_4^-]$ .

### ELECTROLYTIC CELL

- Q.43 Calculate the no. of electrons lost or gained during electrolysis of  
 (a) 3.55 gm of  $\text{Cl}^-$  ions  
 (b) 1 gm  $\text{Cu}^{2+}$  ions  
 (c) 2.7 gm of  $\text{Al}^{3+}$  ions
- Q.44 How many faradays of electricity are involved in each of the case  
 (a) 0.25 mole  $\text{Al}^{3+}$  is converted to  $\text{Al}$ .  
 (b) 24 gm of  $\text{SO}_3$  is converted to  $\text{SO}_3^{2-}$   
 (c) The  $\text{Cu}^{2+}$  in 1100 ml of 0.5 M  $\text{Cu}^{2+}$  is converted to  $\text{Cu}$ .
- Q.45 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.

- Q.46 The electrosynthesis of  $\text{MnO}_2$  is carried out from a solution of  $\text{MnSO}_4$  in  $\text{H}_2\text{SO}_4$  (aq). If a current of 25 ampere is used with a current efficiency of 80%, how long would it take to produce 0.870 kg of  $\text{MnO}_2$ ?
- Q.47 If 0.224 litre of  $\text{H}_2$  gas is formed at the cathode, how much  $\text{O}_2$  gas is formed at the anode under identical conditions?
- Q.48 Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?
- Q.49 Chromium metal can be plated out from an acidic solution containing  $\text{CrO}_3$  according to following equation:  
 $\text{CrO}_3(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cr}(\text{s}) + 3\text{H}_2\text{O}$   
 Calculate :  
 (i) How many grams of chromium will be plated out by 24000 coulombs and  
 (ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current
- Q.50 Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?
- Q.51 How long a current of 2A has to be passed through a solution of  $\text{AgNO}_3$  to coat a metal surface of  $80\text{cm}^2$  with  $5\mu\text{m}$  thick layer? Density of silver =  $10.8\text{g/cm}^3$ .
- Q.52 A metal is known to form fluoride  $\text{MF}_2$ . When 10A of electricity is passed through a molten salt for 330 sec., 1.98g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from  $\text{CuSO}_4$ ?
- Q.53 Cadmium amalgam is prepared by electrolysis of a solution of  $\text{CdCl}_2$  using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2gm Hg (Cd=112.4)
- Q.54 A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode? [Ni = 58.71]
- Q.55 A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of  $\text{Ni}(\text{NO}_3)_2$ . What will be the molarity of solution at the end of electrolysis?
- Q.56 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 mintue. It was found that after electrolysis, the absorbance (concentration) of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.
- Q.57 Electrolysis of a solution of  $\text{HSO}_4^-$  ions produces  $\text{S}_2\text{O}_8^{2-}$ , assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mole of  $\text{S}_2\text{O}_8^{2-}$  per hour?
- Q.58 A current of 3 amp was passed for 2 hour through a solution of  $\text{CuSO}_4$ , 3 g of  $\text{Cu}^{2+}$  ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.



- Q.59 Dal lake has water  $8.2 \times 10^{12}$  litre approximately. A power reactor produces electricity at the rate of  $1.5 \times 10^6$  coulomb per second at an appropriate voltage. How many years would it take to electrolyse the lake?

### CONDUCTANCE

- Q.60 The resistance of a conductivity cell filled with 0.01N solution of NaCl is 210 ohm at  $18^\circ\text{C}$ . Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is  $0.88 \text{ cm}^{-1}$ .
- Q.61 The molar conductivity of 0.1 M  $\text{CH}_3\text{COOH}$  solution is  $4.6 \text{ S cm}^2 \text{ mole}^{-1}$ . What is the specific conductivity and resistivity of the solution?
- Q.62 The conductivity of pure water in a conductivity cell with electrodes of cross sectional area  $4 \text{ cm}^2$  and  $2 \text{ cm}$  apart is  $8 \times 10^{-7} \text{ S cm}^{-1}$ .  
 (i) What is resistance of conductivity cell?  
 (ii) What current would flow through the cell under an applied potential difference of 1 volt?
- Q.63 For 0.01N KCl, the resistivity 709.22 ohm cm. Calculate the conductivity and equivalent conductance.
- Q.64 The resistance of 0.5 M solution of an electrolyte in a cell was found to be 50W. If the electrodes in the cell are  $2.2 \text{ cm}$  apart and have an area of  $4.4 \text{ cm}^2$  then, calculate the molar conductivity (in  $\text{S m}^2 \text{ mol}^{-1}$ ) of the solution.
- Q.65 A solution containing 2.08 g of anhydrous barium chloride is  $400 \text{ cm}^3$  of water has a conductivity  $0.0058 \text{ ohm}^{-1} \text{ cm}^{-1}$ . What are molar and equivalent conductivities of this solution.

### APPLICATION OF KOHLRAUSCH'S LAW

- Q.66 For the strong electrolytes NaOH, NaCl and  $\text{BaCl}_2$  the molar ionic conductivities at infinite dilution are  $248.1 \times 10^{-4}$ ,  $126.5 \times 10^{-4}$  and  $280.0 \times 10^{-4} \text{ mho cm}^2 \text{ mol}^{-1}$  respectively. Calculate the molar conductivity of  $\text{Ba(OH)}_2$  at infinite dilution.
- Q.67 Equivalent conductance of 0.01 N  $\text{Na}_2\text{SO}_4$  solution is  $117 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ . The equivalent conductance at infinite dilution is  $130 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ . What is the degree of dissociation in 0.01 N  $\text{Na}_2\text{SO}_4$  solution?
- Q.68 The value of  $\Lambda_m^\infty$  for HCl, NaCl and  $\text{CH}_3\text{CO}_2\text{Na}$  are 426.1, 126.5 and  $91 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. Calculate the value of  $\Lambda_m^\infty$  for acetic acid. If the equivalent conductivity of the given acetic acid is 48.15 at  $25^\circ\text{C}$ , calculate its degree of dissociation.
- Q.69 Specific conductance of a saturated solution of AgBr is  $8.486 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ . Specific conductance of pure water at  $25^\circ\text{C}$  is  $0.75 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ .  $\Lambda_m^\infty$  for KBr,  $\text{AgNO}_3$  and  $\text{KNO}_3$  are 137.4, 133, 131 ( $\text{S cm}^2 \text{ mol}^{-1}$ ) respectively. Calculate the solubility of AgBr in gm/litre.
- Q.70 Saturated solution of AgCl at  $25^\circ\text{C}$  has specific conductance of  $1.12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The  $\lambda_\infty \text{ Ag}^+$  and  $\lambda_\infty \text{ Cl}^-$  are 54.3 and  $65.5 \text{ ohm}^{-1} \text{ cm}^2 / \text{equi.}$  respectively. Calculate the solubility product of AgCl at  $25^\circ\text{C}$ .



- Q.71 Hydrofluoric acid is weak acid. At 25°C, the molar conductivity of 0.002M HF is  $176.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ . If its  $\Lambda_m^\infty = 405.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ , calculate its degree of dissociation and equilibrium constant at the given concentration.
- Q.72 The equivalent conductance of 0.10 N solution of  $\text{MgCl}_2$  is  $90 \text{ mho cm}^2 \text{ equi}^{-1}$  at 25°C. a cell with electrode that are  $1.5 \text{ cm}^2$  in surface area and 0.5 cm apart is filled with 0.1 N  $\text{MgCl}_2$  solution. How much current will flow when potential difference between the electrodes is 5 volt.
- Q.73 When a solution of specific conductance  $1.2 \text{ ohm}^{-1} \text{ metre}^{-1}$  was placed in a conductivity cell with parallel electrodes, the resistance was found to be 150 ohm. Area of electrodes is  $2 \times 10^{-4} \text{ m}^2$ . Calculate separation of electrodes.
- 
-

## EXERCISE-2

**Single correct**

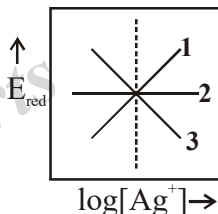
Q.1 The potential of hydrogen electrode in contact with a solution whose pH is 6, pressure of  $H_2$  is 1 bar will

be -[Given :  $\frac{RT(2.303)}{F} = 0.06$  ]

- (A) 0.36 V (B) 0.72V (C) 0.3V (D) 0.21V

Q.2 For half cell reaction :  $Ag^+(aq) + 1e^- \longrightarrow Ag(s)$

Which of the following line represent variation of reduction potential with concentration of  $Ag^+$ ?



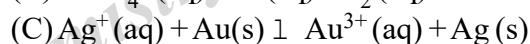
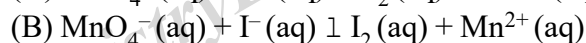
- (A) 1 (B) 2 (C) 3 (D) (A) and (C) both

Q.3 Which of the following reaction is spontaneous?

Given :  $E^\circ_{MnO_4^- / Mn^{2+}} = 1.51 \text{ V}$ ,  $E^\circ_{F^- / F_2} = -2.87 \text{ V}$

$E^\circ_{Au^{3+} / Au} = 1.5 \text{ V}$ ,  $E^\circ_{Ag / Ag^+} = -0.8 \text{ V}$

$E^\circ_{I_2 / I^-} = 0.535 \text{ V}$



(D) All are spontaneous

Q.4 One gm metal  $M^{+2}$  was discharged by the passage of  $1.81 \times 10^{22}$  electrons. What is the atomic weight of metal?

- (A) 33.35 (B) 133.4 (C) 66.7 (D) 55

Q.5 One mole of electron passes through each of the solution of  $AgNO_3$ ,  $CuSO_4$  and  $AlCl_3$  then Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are

- (A) 1 : 1 : 1 (B) 6 : 3 : 2 (C) 6 : 3 : 1 (D) 1 : 3 : 6

Q.6 Salts of A (atomic weight = 7), B (atomic weight = 27) and C (atomic weight = 48) were electrolysed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively are

- (A) 3, 1 and 2 (B) 1, 3 and 2 (C) 3, 1 and 3 (D) 2, 3 and 2

Q.7 The density of Cu is  $8.94 \text{ g cm}^{-3}$ . The quantity of electricity needed to plate an area  $10 \text{ cm} \times 10 \text{ cm}$  to a thickness of  $10^{-2} \text{ cm}$  using  $CuSO_4$  solution would be

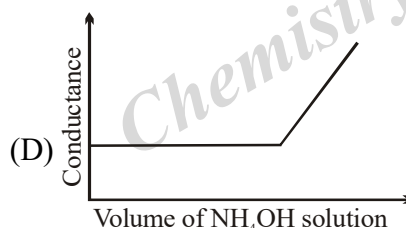
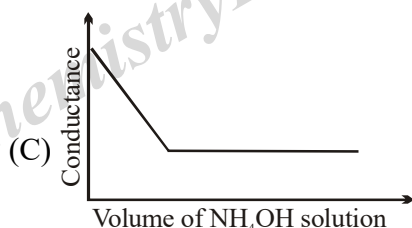
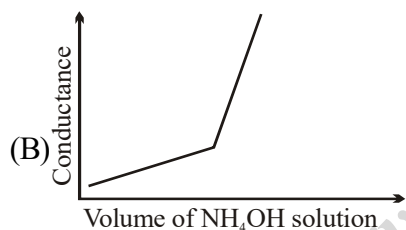
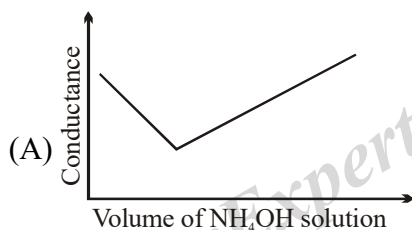
- (A) 13586 C (B) 27172 C (C) 40758 C (D) 20348 C

- Q.8 During electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be  
 (A) 1.2 L (B) 2.4 L (C) 2.6 L (D) 4.8 L
- Q.9 During electrolysis of an aqueous solution of  $\text{CuSO}_4$  using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode  
 (A) 890 ml of  $\text{Cl}_2$  at STP is liberated (B) 445 ml of  $\text{O}_2$  at STP is liberated  
 (C) 2.5 g of copper is deposited (D) a decrease of 2.5 g of mass takes place
- Q.10 A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.  
 (A)  $\text{H}_2$ ,  $\text{O}_2$  (B)  $\text{O}_2$ ,  $\text{H}_2$  (C)  $\text{O}_2$ , Na (D) none
- Q.11 A standard hydrogen electrode has zero electrode potential because  
 (A) hydrogen is easier to oxidise  
 (B) this electrode potential is assumed to be zero  
 (C) hydrogen atom has only one electron  
 (D) hydrogen is the lightest element.
- Q.12 If the pressure of  $\text{H}_2$  gas is increased from 1 atm to 100 atm keeping  $\text{H}^+$  concentration constant at 1 M, the change in reduction potential of hydrogen half cell at  $25^\circ\text{C}$  will be  
 (A) 0.059 V (B) 0.59 V (C) 0.0295 V (D) 0.118 V
- Q.13 For the cell  
 $\text{Pt} | \text{H}_2(0.4 \text{ atm}) | \text{H}^+(\text{pH}=1) || \text{H}^+(\text{pH}=2) | \text{H}_2(0.1 \text{ atm}) | \text{Pt}$   
 The measured potential at  $25^\circ\text{C}$  is  
 (A) -0.1 V (B) -0.5 (C) -0.041 (D) none
- Q.14 For the fuel cell reaction  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l})$ ;  $\Delta_f H_{298}^\circ(\text{H}_2\text{O}, \text{l}) = -285.5 \text{ kJ/mol}$   
 What is  $\Delta S_{298}^\circ$  for the given fuel cell reaction?  
 Given:  $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$   $E^\circ = 1.23 \text{ V}$   
 (A) -0.322 J/K (B) -0.635 kJ/K (C) 3.51 kJ/K (D) -0.322 kJ/K
- Q.15 The standard reduction potentials of  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Cu}^{2+}/\text{Cu}^+$  are 0.337 and 0.153 V respectively. The standard electrode potential of  $\text{Cu}^+/\text{Cu}$  half cell is  
 (A) 0.184 V (B) 0.827 V (C) 0.521 V (D) 0.490 V
- Q.16 The resistance of 0.5 M solution of an electrolyte in a cell was found to be  $50 \Omega$ . If the electrodes in the cell are 2.2 cm apart and have an area of  $4.4 \text{ cm}^2$  then the molar conductivity (in  $\text{S m}^2 \text{mol}^{-1}$ ) of the solution is  
 (A) 0.2 (B) 0.02 (C) 0.002 (D) None of these
- Q.17 Equivalent conductance of 0.1 M HA (weak acid) solution is  $10 \text{ Scm}^2 \text{equivalent}^{-1}$  and that at infinite dilution is  $200 \text{ Scm}^2 \text{equivalent}^{-1}$  Hence pH of HA solution is  
 (A) 1.3 (B) 1.7 (C) 2.3 (D) 3.7

- Q.18 The electrical resistance of a column of  $0.07 \text{ mol L}^{-1}$  NaOH solution of diameter 1 cm and length 55 cm is  $5 \times 10^3 \text{ ohm}$ . What will be its molar conductivity.  $\left(\pi = \frac{22}{7}\right)$   
 (A)  $50 \text{ S cm}^2 \text{ mol}^{-1}$  (B)  $100 \text{ S cm}^2 \text{ mol}^{-1}$  (C)  $150 \text{ S cm}^2 \text{ mol}^{-1}$  (D)  $200 \text{ S cm}^2 \text{ mol}^{-1}$
- Q.19 If the conductivity of  $0.001 \text{ M}$  propionic acid is  $3.83 \times 10^{-5} \text{ S cm}^{-1}$  and limiting molar conductivities of HCl, KCl and potassium propionate are 426, 126,  $83 \text{ S cm}^2 \text{ mol}^{-1}$  respectively then acid dissociation constant of propionic acid is -  
 (A)  $10^{-6}$  (B)  $1.11 \times 10^{-5}$  (C)  $1.11 \times 10^{-4}$  (D)  $10^{-3}$
- Q.20 If  $x$  is specific resistance of the electrolyte solution and  $y$  is the molarity of the solution, then  $\wedge_m$  is given by [ $x$  is in  $\text{ohm cm}^{-1}$  &  $\lambda_m$  in  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ]  
 (A)  $\frac{1000x}{y}$  (B)  $1000 \frac{y}{x}$  (C)  $\frac{1000}{xy}$  (D)  $\frac{xy}{1000}$
- Q.21 The dissociation constant of n-butyric acid is  $1.6 \times 10^{-5}$  and the molar conductivity at infinite dilution is  $380 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$ . The specific conductance of the  $0.01 \text{ M}$  acid solution is  
 (A)  $1.52 \times 10^{-5} \text{ Sm}^{-1}$  (B)  $1.52 \times 10^{-2} \text{ Sm}^{-1}$   
 (C)  $1.52 \times 10^{-3} \text{ Sm}^{-1}$  (D) None
- Q.22 The conductivity of a saturated solution of  $\text{Ag}_3\text{PO}_4$  is  $9 \times 10^{-6} \text{ S m}^{-1}$  and its equivalent conductivity is  $1.50 \times 10^{-4} \text{ S m}^2 \text{ equivalent}^{-1}$ . The  $K_{sp}$  of  $\text{Ag}_3\text{PO}_4$  is  
 (A)  $4.32 \times 10^{-18}$  (B)  $1.8 \times 10^{-9}$  (C)  $8.64 \times 10^{-13}$  (D) None of these
- Q.23 A saturated solution in AgA ( $K_{sp} = 3 \times 10^{-14}$ ) and AgB ( $K_{sp} = 1 \times 10^{-14}$ ) has conductivity of  $375 \times 10^{-10} \text{ Scm}^{-1}$  and limiting molar conductivity of  $\text{Ag}^+$  and  $\text{A}^-$  are  $60 \text{ Scm}^2 \text{ mol}^{-1}$  and  $80 \text{ Scm}^2 \text{ mol}^{-1}$  respectively then what will be the limiting molar conductivity of  $\text{B}^-$  (in  $\text{Scm}^2 \text{ mol}^{-1}$ )  
 (A) 150 (B) 180 (C) 190 (D) 270
- Q.24 The solubility of AB if  $\lambda_{A^+}^{\circ} = 50 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ,  $\lambda_{B^-}^{\circ} = 70 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$  and the measured resistance was  $33.5 \Omega$  in a cell with cell constant of  $0.2 \text{ cm}^{-1}$  is :  
 (A) 59.7 millimoles/L (B) 49.7 millimoles/L  
 (C) 39.7 millimoles/L (D) 29.7 millimoles/L
- Q.25 Equal volumes of  $0.015 \text{ M CH}_3\text{COOH}$  &  $0.015 \text{ M NaOH}$  are mixed together. What would be molar conductivity of mixture if conductivity of  $\text{CH}_3\text{COONa}$  is  $6.3 \times 10^{-4} \text{ S cm}^{-1}$   
 (A)  $8.4 \text{ S cm}^2 \text{ mol}^{-1}$  (B)  $84 \text{ S cm}^2 \text{ mol}^{-1}$   
 (C)  $4.2 \text{ S cm}^2 \text{ mol}^{-1}$  (D)  $42 \text{ S cm}^2 \text{ mol}^{-1}$
- Q.26 A gas Y at 1 atm is bubbled through a solution containing a mixture of  $1 \text{ M X}$  and  $1 \text{ M Z}$  at  $25^\circ\text{C}$ . If the reduction potential of  $\text{Z} > \text{Y} > \text{X}$ , then  
 (A) Y will oxidise X and not Z (B) Y will oxidise Z and X  
 (C) Y will oxidise both X and Z (D) Y will reduce both X and Z.

- Q.27 For the electrochemical cell,  $M | M^+ || X^- | X$ ,  $E^\circ (M^+/M) = 0.44 \text{ V}$  and  $E^\circ (X/X^-) = 0.33 \text{ V}$ . From this data, one can deduce that
- (A)  $M + X \longrightarrow M^+ + X^-$  is the spontaneous reaction  
 (B)  $M^+ + X^- \longrightarrow M + X$  is the spontaneous reaction  
 (C)  $E_{\text{cell}} = 0.77 \text{ V}$   
 (D)  $E_{\text{cell}} = -0.77 \text{ V}$

- Q.28 In the conductometric titration, the conductance is measured at different stages on adding some volume of the standard solution and then a graph is plotted to get end point. Which of the following plots will be obtained for a conductometric titration of  $\text{HCl}$  against  $\text{NH}_4\text{OH}$ ?

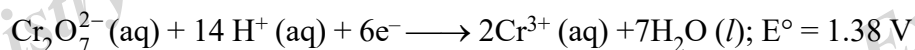
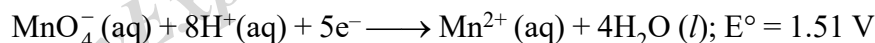


- Q.29 The correct order of equivalent conductance at infinite dilution of  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$  is
- (A)  $\text{LiCl} > \text{NaCl} > \text{KCl}$  (B)  $\text{KCl} > \text{NaCl} > \text{LiCl}$   
 (C)  $\text{NaCl} > \text{KCl} > \text{LiCl}$  (D)  $\text{LiCl} > \text{KCl} > \text{NaCl}$

- Q.30 Saturated solution of  $\text{KNO}_3$  is used to make salt bridge because

- (A) velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$   
 (B) velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$   
 (C) velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same  
 (D)  $\text{KNO}_3$  is highly soluble in water

- Q.31 Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:



Identify the only incorrect statement regarding quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$

- (A)  $\text{MnO}_4^-$  can be used in aqueous  $\text{HCl}$  (B)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{HCl}$   
 (C)  $\text{MnO}_4^-$  can be used in aqueous  $\text{H}_2\text{SO}_4$  (D)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{H}_2\text{SO}_4$

**More than one may be correct :**

Q.32 Which of the following arrangement will produce oxygen at anode during electrolysis ?

- (A) Dilute  $\text{H}_2\text{SO}_4$  solution with Cu electrodes.
- (B) Dilute  $\text{H}_2\text{SO}_4$  solution with inert electrodes.
- (C) Fused NaOH with inert electrodes.
- (D) Dilute NaCl solution with inert electrodes.

Q.33 Identify the **correct** statement :

- (A) Molar conductance ( $\lambda_m$ ) is intensive quantity.
- (B) During discharging of lead storage battery density of electrolyte solution decrease.
- (C) Cell constant values of a cell are independent of electrolyte used.
- (D) Fresh water corrodes much faster than sea water.

Q.34 Following data is obtained for aqueous solution of NaCl at  $25^\circ\text{C}$

|                                                            |       |       |
|------------------------------------------------------------|-------|-------|
| conc.(M)                                                   | 0.25  | 1.00  |
| $\Lambda_m$ ( $\text{ohm}^{-1}\text{m}^2\text{mol}^{-1}$ ) | 0.016 | 0.015 |

Identify the **correct** statement(s) regarding the solution at  $25^\circ\text{C}$  :

- (A) The value of  $\Lambda_m^\infty$  is  $0.017 \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$ .
- (B) The value of  $\Lambda_m$  for 0.16 M - NaCl solution is  $0.0162 \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$ .
- (C) The conductivity of 0.04 M - NaCl solution is  $0.664 \text{ ohm}^{-1} \text{ m}^{-1}$ , when the conductivity of water is neglected.
- (D) Conductivity of NaCl solution increases on dilution.

Q.35 The limiting molar conductance  $\lambda_m^0$  of HCl, NaCl and  $\text{CH}_3\text{COONa}$  is given by 430, 120 &  $90 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. If conductance of a 0.1 M solution of  $\text{CH}_3\text{COOH}$  is  $4 \times 10^{-3} \text{ S}$  in a conducting cell of cell constant  $\frac{1}{10} \text{ cm}^{-1}$  then identify the correct statement(s).

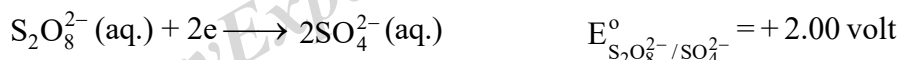
- (A) Specific conductance of 0.1 M  $\text{CH}_3\text{COOH}$  solution is  $4 \times 10^{-4} \text{ S cm}^{-1}$
- (B) pH of 0.1 M  $\text{CH}_3\text{COOH}$  solution is 3.
- (C) Degree of dissociation of  $\text{CH}_3\text{COOH}$  1%.
- (D) Specific conductance of 0.2 M solution of  $\text{CH}_3\text{COOH}$  will be less than  $3 \times 10^{-4} \text{ S cm}^{-1}$

Q.36 Choose the correct statement(s).

- (A) Cell constant values of conductivity cells are independent of the solution filled into the cell.
- (B) Kohlrausch law is valid for strong electrolyte but not for weak electrolyte
- (C) In general conductivity decreases on dilution whereas equivalent and molar conductivity increase on dilution.
- (D) Salt bridge is employed to maintain the electrical neutrality and to minimize the liquid - liquid junction potential.

- Q.37 If 270.0 g of water is electrolysed during an experiment performed by miss Abhilasha with 75% current efficiency then
- (A) 168 L of  $O_2$  (g) will be evolved at anode at 1 atm & 273 K
- (B) Total 504 L gases will be produced at 1 atm & 273 K.
- (C) 336 L of  $H_2$  (g) will be evolved at anode at 1 atm & 273 K
- (D) 45 F electricity will be consumed

- Q.38 Pick out the **correct** statements among the following from inspection of standard reduction potentials (**Assume** standard state conditions).



- (A)  $Cl_2$  can oxidise  $SO_4^{2-}$  from solution
- (B)  $Cl_2$  can oxidise  $Br^-$  and  $I^-$  from aqueous solution
- (C)  $S_2O_8^{2-}$  can oxidise  $Cl^-$ ,  $Br^-$  and  $I^-$  from their aqueous solutions
- (D)  $S_2O_8^{2-}$  is added slowly,  $Br^-$  can be reduce in presence of  $Cl^-$
- Q.39 The EMF of the following cell is 0.22 volt.
- $Ag(s) | AgCl(s) | KCl(1M) | H^+(1M) | H_2(g)(1atm) ; Pt(s).$
- Which of the following will decrease the EMF of cell.
- (A) increasing pressure of  $H_2(g)$  from 1 atm to 2 atm
- (B) increasing  $Cl^-$  concentration in Anodic compartment
- (C) increasing  $H^+$  concentration in cathodic compartment
- (D) decreasing KCl concentration in Anodic compartment.

### Assertion & Reasoning type questions

- Q.40 **Statement -1** : The voltage of mercury cell remains constant for long period of time.
- Statement -2** : It is because net cell reaction does not involve active species.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.
- Q.41 **Statement -1** : The SRP of three metallic ions  $A^+$ ,  $B^{2+}$ ,  $C^{3+}$  are  $-0.3, -0.5, 0.8$  volt respectively, so oxidising power of ions is  $C^{3+} > A^+ > B^{2+}$ .
- Statement -2** : Higher the SRP, higher the oxidising power.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.



- Q.42 **Statement -1** : We can add the electrode potential in order to get electrode potential of net reaction.  
**Statement -2** : Electrode potential is an intensive property.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**Comprehension :**

**Paragraph for Question Nos. 43 to 45**

A sample of water from a large swimming pool has a resistance of  $10000\ \Omega$  at  $25^\circ\text{C}$  when placed in a certain conductance cell. When filled with  $0.02\ \text{M}$  KCl solution, the cell has a resistance of  $100\ \Omega$  at  $25^\circ\text{C}$ .  $585\ \text{gm}$  of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of  $8000\ \Omega$ . [Given : Molar conductance of NaCl at that concentration is  $125\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$  and molar conductivity of KCl at  $0.02\ \text{M}$  is  $200\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ .]

- Q.43 Cell constant (in  $\text{cm}^{-1}$ ) of conductance cell is:  
 (A) 4 (B) 0.4 (C)  $4 \times 10^{-2}$  (D)  $4 \times 10^{-5}$
- Q.44 Conductivity ( $\text{S cm}^{-1}$ ) of  $\text{H}_2\text{O}$  is:  
 (A)  $4 \times 10^{-2}$  (B)  $4 \times 10^{-3}$  (C)  $4 \times 10^{-5}$  (D) None of these
- Q.45 Volume (in Litres) of water in the pool is:  
 (A)  $1.25 \times 10^5$  (B) 1250 (C) 12500 (D) None of these

**Match the column :**

- Q.51
- | Column I                          | Column II                                    |
|-----------------------------------|----------------------------------------------|
|                                   | (Electrolysis product using inert electrode) |
| (A) Dilute solution of HCl        | (P) $\text{O}_2$ evolved at anode            |
| (B) Dilute solution of NaCl       | (Q) $\text{H}_2$ evolved at cathode          |
| (C) Concentrated solution of NaCl | (R) $\text{Cl}_2$ evolved at anode           |
| (D) $\text{AgNO}_3$ solution      | (S) Ag deposition at cathode                 |

- Q.53
- | Column-I                              | Column-II                        |
|---------------------------------------|----------------------------------|
| (A) Molar conductance ( $\lambda_m$ ) | (P) intensive property           |
| (B) $\frac{\Delta G^\circ}{nF}$       | (Q) extensive property           |
| (C) Conductivity (K) of cell          | (R) increases with dilution      |
| (D) $\Delta G^\circ_{\text{cell}}$    | (S) temperature dependent        |
|                                       | (T) increases with concentration |

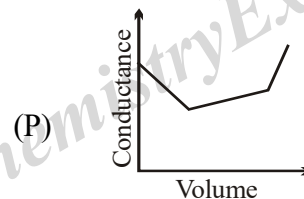


Q.52

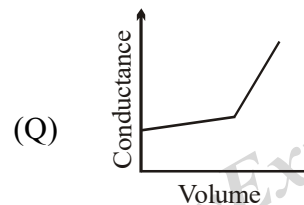
**List-I**  
(Solutions mixed)**List-II**

(Conductance vs Volume of solution added curve)

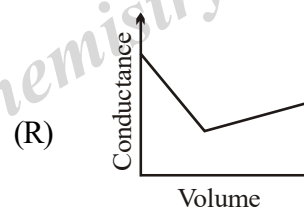
(A) When NaOH solution is added to a solution containing equimolar mixture of  $\text{HCl} + \text{CH}_3\text{COOH}$



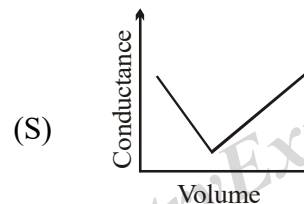
(B)  $\text{BaCl}_2$  solution is added to  $\text{Na}_2\text{SO}_4$  solution



(C)  $\text{NaHCO}_3$  solution is added to  $\text{HCl}$  solution



(D)  $\text{CaCl}_2$  solution is added to  $\text{NaOH}$  solution



(Assume  $\text{Ca(OH)}_2$  is completely insoluble in water)

**ANSWER KEY****EXERCISE-1**

- Q.1 1.61 V      Q.2 1.35 V      Q.3 No
- Q.4 0.53 V, undergo disproportionation      Q.5  $-0.04 \text{ V}$
- Q.6 0.1 V      Q.7 0.522 V, 0.613 V      Q.8  $K_c = 4.68 \times 10^{12}$
- Q.9  $K_c = 7.94 \times 10^{25}$       Q.10  $E^0 = 0.7835 \text{ V}$       Q.11  $10^{-2}$
- Q.12  $E = 1.159 \text{ V}$       Q.13  $K_c = 1.0 \times 10^{106}$ ,  $\Delta G^0 = -613.74 \text{ kJ}$
- Q.14  $n = 2$       Q.15 No,  $E_{\text{cell}} = -0.078 \text{ V}$       Q.16  $[\text{Cu}^{2+}] = 4.68 \times 10^{-12} \text{ M}$
- Q.17 0.62 V      Q.18 0.05 M      Q.19 4
- Q.20  $K_a = 3.2 \times 10^{-3}$       Q.21 1.414 V      Q.22  $E = -0.81 \text{ V}$
- Q.23 0.0295 V      Q.24  $E = 0.059 / \text{V}$       Q.25  $E = 0.402 \text{ V}$
- Q.26  $\text{pH} = 4$       Q.27  $-0.42 \text{ V}$       Q.28  $E^0 = -0.23 \text{ V}$
- Q.29 (ii). 1.27 V, (iii) 245.1 kJ      Q.30  $[\text{Br}^-] : [\text{Cl}^-] = 1 : 200$
- Q.31  $E^0 = -0.19 \text{ V}$       Q.32 0.3 Volt      Q.33  $10^{-15}$
- Q.34  $-0.74 \text{ Volt}$       Q.35  $-0.036 \text{ V}$       Q.36 1.1 V
- Q.37  $10^{-5} \text{ M}^3$       Q.38  $K_{\text{sp}} = 2.287 \times 10^{-12}$
- Q.39  $\Delta H^0 = -49987 \text{ J mol}^{-1}$ ,  $\Delta S^0 = -96.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $s = 1.47 \times 10^{-5} \text{ M}$
- Q.40  $K = 10^{268}$       Q.41  $K_c = 6.26 \times 10^7$       Q.42  $-1.30 \times 10^3 \text{ kJ mol}^{-1}$
- Q.43 (a)  $6.02 \times 10^{22}$  electrons lost, (b)  $1.89 \times 10^{22}$  electrons gained, (c) (b)  $1.80 \times 10^{23}$  electrons gained
- Q.44 (a) 0.75 F, (b) 0.6 F, (c) 1.1 F      Q.45 (i) 54 gm, (ii) 16.35 gm
- Q.46 96500 sec      Q.47 0.112 litre      Q.48 Rs. 0.75 x
- Q.49 (i) 2.1554 gm ; (ii) 1336.15 sec      Q.50 115800 C, 347.4 kJ
- Q.51  $t = 193 \text{ sec}$       Q.52  $A = 115.8$ ,  $Q = 6018 \text{ C}$       Q.53  $t = 93.65 \text{ sec.}$
- Q.54 1.825 g      Q.55 2M      Q.56  $7.95 \times 10^{-5} \text{ M}$

- Q.57 71.5 Amp                      Q.58 42.2 %                      Q.59 1.9 million year
- Q.60  $419 \text{ S cm}^2 \text{ equivalent}^{-1}$                       Q.61  $0.00046 \text{ S cm}^{-1}$  ;  $2174 \text{ ohm cm}$
- Q.62 (i)  $6.25 \times 10^5 \text{ ohm}$ , (ii)  $1.6 \times 10^{-6} \text{ amp}$
- Q.63  $0.0141 \text{ mho g equiv}^{-1} \text{ m}^2$ ,  $0.141 \text{ mho m}^{-1}$                       Q.64 0.002
- Q.65 (i)  $232 \text{ Mho cm}^2 \text{ mol}^{-1}$ , (ii)  $116 \text{ Mho cm}^2 \text{ equivalent}^{-1}$
- Q.66  $523.2 \times 10^{-4} \text{ mho cm}^2 \text{ mol}^{-1}$                       Q.67 0.9
- Q.68 (i)  $390.6 \text{ S cm}^2 \text{ mol}^{-1}$  (ii) 12.32%
- Q.70  $8.74 \times 10^{-11} \text{ mole}^2 / \text{litre}^2$                       Q.71  $\alpha = 0.435$ ,  $k = 6.7 \times 10^{-4}$
- Q.72 0.135 ampere                      Q.73  $3.6 \times 10^{-2} \text{ metre}$

**EXERCISE-2**

- Q.1 A                      Q.2 A                      Q.3 B                      Q.4 C                      Q.5 B
- Q.6 B                      Q.7 B                      Q.8 D                      Q.9 D                      Q.10 A
- Q.11 B                      Q.12 A                      Q.13 C                      Q.14 D                      Q.15 C
- Q.16 C                      Q.17 C                      Q.18 D                      Q.19 B                      Q.20 C
- Q.21 B                      Q.22 A                      Q.23 D                      Q.24 B                      Q.25 B
- Q.26 A                      Q.27 B                      Q.28 C                      Q.29 B                      Q.30 C
- Q.31 A                      Q.32 BCD                      Q.33 ABC                      Q.34 ABC                      Q.35 ABC
- Q.36 ACD                      Q.37 AB                      Q.38 BC                      Q.39 AD                      Q.40 A
- Q.41 A                      Q.42 D                      Q.43 B                      Q.44 C                      Q.45 A
- Q.46 (A) P, Q (B) P, Q (C) Q, R, (D) P,S
- Q.47 (A) PRS (B) PS (C) PST (D)QS
- Q.48 (A) P (B) Q (C) R (D) S

**EXERCISE-1 (Subjective Questions)****Ionization Constants and pH**

- Q.1 Calculate the number of  $H^+$  present in one ml of solution whose pH is 13.
- Q.2 Calculate change in concentration of  $H^+$  ion in one litre of water, when temperature changes from 298 K to 310 K. Given  $K_w(298) = 10^{-14}$   $K_w(310) = 2.56 \times 10^{-14}$ .
- Q.3 (i)  $K_w$  for  $H_2O$  is  $9.62 \times 10^{-14}$  at  $60^\circ C$ . What is pH of water at  $60^\circ C$ .  
 (ii) What is the nature of solution at  $60^\circ C$  whose  
 (a) pH = 6.7 (b) pH = 6.35
- Q.4 The value of  $K_w$  at the physiological temperature ( $37^\circ C$ ) is  $2.56 \times 10^{-14}$ . What is the pH at the neutral point of water at this temperature?
- Q.5 Calculate pH of following solutions :  
 (a) 0.1 M HCl  
 (b) 0.1 M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ )  
 (c) 0.1 M  $NH_4OH$  ( $K_b = 1.8 \times 10^{-5}$ )  
 (d)  $10^{-8}$  M HCl  
 (e)  $10^{-10}$  M NaOH  
 (f)  $10^{-8}$  M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ )  
 (g) Decimolar solution of Baryta [ $Ba(OH)_2$ ], diluted 100 times.  
 (h)  $10^{-3}$  mole of KOH dissolved in 100 L of water.  
 (i) equal volume of HCl solution (pH = 4) + 0.0019 N HCl solution  
 (j)  $10^{-7}$  M NaOH
- Q.6 Calculate :  
 (a)  $K_a$  for a monobasic acid whose 0.10 M solution has pH of 4.50.  
 (b)  $K_b$  for a monoacidic base whose 0.10 M solution has a pH of 10.50.
- Q.7 Calculate the ratio of degree of dissociation ( $\alpha_2/\alpha_1$ ) when 1 M acetic acid solution is diluted to 100 times. [Given  $K_a = 10^{-5}$ ]
- Q.8 Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids. [Given  $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ ;  $K_a(HCN) = 6.2 \times 10^{-10}$ ]
- Q.9 pH of a dilute solution of HCl is 6.95. Calculate molarity of HCl solution.
- Q.10 The pH of aqueous solution of ammonia is 12. Find molarity of solution.  $K_b(NH_4OH) = 10^{-5}$ .
- Q.11 The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate  $K_a$  of weak acid.
- Q.12 Boric acid is a weak monobasic acid. It ionizes in water as  

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ : K_a = 5.9 \times 10^{-10}$$
 Calculate pH of 0.3 M boric acid.

- Q.13 What is the pH of a 1.0 M solution of acetic acid ? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value. Given  $K_a = 1.8 \times 10^{-5}$ .

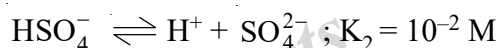
**Mixture of two or more acids / bases**

- Q.14 Calculate pH of following solutions :  
 (a) 0.08 M  $H_2SO_4$  (50 ml) + 0.04 M HCl 50 (ml)  
 (b) 0.1 M HA + 0.1 M HB [  $K_a$  (HA) =  $2 \times 10^{-5}$  ;  $K_a$  (HB) =  $4 \times 10^{-5}$  ]
- Q.15 Calculate  $[H^+]$  and  $[CHCl_2COO^-]$  in a solution that is 0.01 M in HCl and 0.01 M in  $CHCl_2COOH$ . Take ( $K_a = 2.55 \times 10^{-2}$ ).
- Q.16 Calculate  $[H^+]$ ,  $[CH_3COO^-]$  and  $[C_7H_5O_2^-]$  in a solution that is 0.02 M in acetic acid and 0.01M in benzoic acid.  $K_a$  (acetic) =  $1.8 \times 10^{-5}$ ,  $K_a$  (benzoic) =  $6.4 \times 10^{-5}$ .

**Polyprotic acids & bases**

- Q.17 What are the concentration of  $H^+$ ,  $H_2C_2O_4$ ,  $HC_2O_4^-$  and  $C_2O_4^{2-}$  in a 0.1 M solution of oxalic acid ?  
 [ $K_1 = 10^{-2}$  and  $K_2 = 10^{-5}$  ]
- Q.18 What are the concentrations of  $H^+$ ,  $HSO_4^-$ ,  $SO_4^{2-}$  and  $H_2SO_4$  in a 0.20 M solution of sulphuric acid ?

Given:  $H_2SO_4 \longrightarrow H^+ + HSO_4^-$  ; strong



**Hydrolysis**

- Q.19 What is the  $OH^-$  concentration of a 0.08 M solution of  $CH_3COONa$ . [ $K_a$  ( $CH_3COOH$ ) =  $1.8 \times 10^{-5}$ ]
- Q.20 Calculate the pH of a 0.1 M solution of  $NH_4Cl$ . [ $K_b$  ( $NH_3$ ) =  $10^{-5}$ ]
- Q.21 0.252 M solution of pyridinium chloride  $C_5H_6N^+Cl^-$  was found to have a pH of 2.699. What is  $K_b$  for pyridine,  $C_5H_5N$  ?
- Q.22 Calculate the extent of hydrolysis & the pH of 0.02 M  $CH_3COONH_4$ .  
 [ $K_b$  ( $NH_3$ ) =  $1.8 \times 10^{-5}$ ,  $K_a$  ( $CH_3COOH$ ) =  $1.8 \times 10^{-5}$ ]
- Q.23 Calculate the pH of  $1.0 \times 10^{-3}$  M sodium phenolate, ( $NaOC_6H_5$ ).  $K_a$  for  $HOC_6H_5$  is  $1.05 \times 10^{-10}$ .
- Q.24 Calculate the percent hydrolysis in a 0.06 M solution of KCN. [ $K_a$  (HCN) =  $6 \times 10^{-10}$ ]
- Q.25 Calculate the percent hydrolysis in a 0.0100 M solution of KCN. ( $K_a = 6.2 \times 10^{-10}$ )
- Q.26 The acid ionization (hydrolysis) constant of  $Zn^{2+}$  is  $1.0 \times 10^{-9}$   
 (a) Calculate the pH of a 0.001 M solution of  $ZnCl_2$   
 (b) What is the basic dissociation constant of  $Zn(OH)^+$ ?
- Q.27 Equal volume of 0.2 M  $CH_3COOH$  is mixed with 0.2 N NaOH solution then find the pH of resultant solution [ $K_a$  ( $CH_3COOH$ ) =  $10^{-5}$ ]

Buffer solution

- Q.28 Determine  $[\text{OH}^-]$  of a 0.050 M solution of ammonia to which sufficient  $\text{NH}_4\text{Cl}$  has been added to make the total  $[\text{NH}_4^+]$  equal to 0.100.  $[K_b(\text{NH}_3) = 1.8 \times 10^{-5}]$
- Q.29 Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M  $\text{CH}_3\text{COOH}$  and 50.0 mL of 0.100 M  $\text{NaOH}$ .  $[K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}]$
- Q.30 A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If  $\text{p}K_b$  of ammonia is 4.74, calculate value of x.
- Q.31 50 mL of 0.1 M  $\text{NaOH}$  is added to 75 mL of 0.1 M  $\text{NH}_4\text{Cl}$  to make a basic buffer. If  $\text{p}K_a$  of  $\text{NH}_4^+$  is 9.26, calculate pH.
- Q.32 (a) Determine the pH of a 0.2 M solution of pyridine  $\text{C}_5\text{H}_5\text{N}$ .  $K_b = 1.5 \times 10^{-9}$   
 (b) Predict the effect of addition of pyridinium ion  $\text{C}_5\text{H}_5\text{NH}^+$  on the position of the equilibrium. Will the pH be raised or lowered?  
 (c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chloride  $\text{C}_5\text{H}_5\text{NH}^+\text{Cl}$ , has been added, assuming no change in volume.
- Q.33 Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M  $\text{HCl}$  with 50.0 ml of 0.4 M  $\text{NH}_3$ .  $[K_b(\text{NH}_3) = 1.8 \times 10^{-5}]$
- Q.34 Calculate the pH of a solution made by mixing 50.0 ml of 0.2M  $\text{NH}_4\text{Cl}$  & 75.0 ml of 0.1 M  $\text{NaOH}$ .  $[K_b(\text{NH}_3) = 1.8 \times 10^{-5}]$

Indicators & titrations

- Q.35 For the indicator thymol blue, pH is 2.0 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with  $[\text{H}^+] = 4 \times 10^{-3} \text{ M}$ .
- Q.36 The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50 % of the new indicator is in ionic form.
- Q.37 Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M  $\text{NH}_3$  with 0.40M  $\text{HCl}$ .  $[K_b = 1.8 \times 10^{-5}]$
- Q.38  $\text{CH}_3\text{COOH}$  (50 ml, 0.1 M) is titrated against 0.1 M  $\text{NaOH}$  solution. Calculate the pH at the addition of 0 ml, 10 ml, 20 ml, 25 ml, 40 ml, 50 ml of  $\text{NaOH}$ .  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $2 \times 10^{-5}$ .
- Q.39 A weak base (50.0mL) was titrated with 0.1 M  $\text{HCl}$ . The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate  $K_b$  of the base and pH at the equivalence point.
- Q.40 A weak acid (50.0mL) was titrated with 0.1 M  $\text{NaOH}$ . The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate  $K_a$  of the acid and pH at the equivalence point.

- Q.41 What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ?
- Q.42 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.  
 (a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.  
 (b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing.  $K_a$  of acetic acid is  $1.75 \times 10^{-5}$  M. ( $\log(1.75) = 0.243$ )

**Solubility & solubility product's**

- Q.43 The values of  $K_{sp}$  for the slightly soluble salts MX and  $QX_2$  are each equal to  $4.0 \times 10^{-18}$ . Which salt is more soluble? Explain your answer fully.
- Q.44 The solubility of  $PbSO_4$  in water is 0.038 g/L. Calculate the solubility product of  $PbSO_4$ .
- Q.45 How many mol CuI ( $K_{sp} = 5 \times 10^{-12}$ ) will dissolve in 1.0 L of 0.10 M NaI solution ?
- Q.46 A solution of saturated  $CaF_2$  is found to contain  $4.1 \times 10^{-4}$  M fluoride ion. Calculate the  $K_{sp}$  of  $CaF_2$ . Neglect hydrolysis.
- Q.47 The solubility of  $ML_2$  (formula weight, 60 g/mol) in water is  $2.4 \times 10^{-5}$  g/100 mL solution. Calculate the solubility product constant for  $ML_2$ .
- Q.48 What is the solubility (in mol/L) of  $Fe(OH)_3$  in a solution of pH = 8.0 ? [ $K_{sp}$  for  $Fe(OH)_3 = 1.0 \times 10^{-36}$ ]
- Q.49 Calculate the solubility of  $A_2X_3$  in pure water, assuming that neither kind of ion reacts with water. For  $A_2X_3$ , [ $K_{sp} = 1.1 \times 10^{-23}$ ]
- Q.50 Determine the solubility of AgCl in 0.1 M  $BaCl_2$ . [ $K_{sp}$  for AgCl =  $1 \times 10^{-10}$ ]
- Q.51 What mass of  $Pb^{2+}$  ion is left in solution when 50.0 mL of 0.20M  $Pb(NO_3)_2$  is added to 50.0 mL of 1.5 M NaCl ? [Given  $K_{sp}$  for  $PbCl_2 = 1.7 \times 10^{-4}$ ]
- Q.52 A solution has a  $Mg^{2+}$  concentration of 0.0010 mol/L. Will  $Mg(OH)_2$  precipitate if the  $OH^-$  concentration of the solution is [ $K_{sp} = 1.2 \times 10^{-11}$ ]  
 (a)  $10^{-5}$  mol/L (b)  $10^{-3}$  mol/L ?
- Q.53 The solubility of  $Pb(OH)_2$  in water is  $6.7 \times 10^{-6}$  M. Calculate the solubility of  $Pb(OH)_2$  in a buffer solution of pH = 10.

**Simultaneous Solubility**

- Q.54 Calculate the Simultaneous solubility of AgSCN and AgBr.  $K_{sp}$  (AgSCN) =  $1.1 \times 10^{-12}$ ,  $K_{sp}$  (AgBr) =  $5 \times 10^{-13}$ .
- Q.55 Calculate  $F^-$  in a solution saturated with respect of both  $MgF_2$  and  $SrF_2$ .  $K_{sp}$  ( $MgF_2$ ) =  $9.5 \times 10^{-9}$ ,  $K_{sp}$  ( $SrF_2$ ) =  $4 \times 10^{-9}$ .

**complexation equilibria**

- Q.56 A recent investigation of the complexation of  $SCN^-$  with  $Fe^{3+}$  led of 130, 16, and 1.0 for  $K_1$ ,  $K_2$ , and  $K_3$ , respectively. What is the overall formation constant of  $Fe(SCN)_3$  from its component ions, and what is the dissociation constant of  $Fe(SCN)_3$  into its simplest ions on the basis of these data ?
- Q.57 How much AgBr could dissolve in 1.0 L of 0.40 M  $NH_3$  ? Assume that  $Ag(NH_3)_2^+$  is the only complex formed. [ $K_f$  ( $Ag(NH_3)_2^+$ ) =  $1 \times 10^8$ ;  $K_{sp}$  (AgBr) =  $5 \times 10^{-13}$ ]



## EXERCISE-2 (Objective Questions)

## Single correct

- Q.1 The conjugate acid of  $\text{NH}_2^-$  is  
 (A)  $\text{NH}_3$  (B)  $\text{NH}_2\text{OH}$  (C)  $\text{NH}_4^+$  (D)  $\text{N}_2\text{H}_4$
- Q.2 Out of the following, amphiprotic species are  
 I  $\text{HPO}_3^{2-}$  II  $\text{OH}^-$  III  $\text{H}_2\text{PO}_4^-$  IV  $\text{HCO}_3^-$   
 (A) I, III, IV (B) I and III (C) III and IV (D) All
- Q.3 pH of an aqueous solution of NaCl at  $85^\circ\text{C}$  should be  
 (A) 7 (B)  $> 7$  (C)  $< 7$  (D) 0
- Q.4 1 cc of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be  
 (A) 7 (B) 3 (C) 4 (D) 1
- Q.5 10 ml of  $\frac{M}{200} \text{H}_2\text{SO}_4$  is mixed with 40 ml of  $\frac{M}{200} \text{H}_2\text{SO}_4$ . The pH of the resulting solution is  
 (A) 1 (B) 2 (C) 2.3 (D) none of these
- Q.6 If  $\text{p}K_b$  for fluoride ion at  $25^\circ\text{C}$  is 10, the ionisation constant of hydrofluoric acid in water at this temperature is:  
 (A)  $1.74 \times 10^{-5}$  (B)  $3.52 \times 10^{-3}$  (C)  $10^{-4}$  (D)  $5.38 \times 10^{-2}$
- Q.7 The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is  
 (A) 1 (B) 2 (C) 3 (D) 11
- Q.8 Which of the following solution will have pH close to 1.0?  
 (A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH  
 (B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH  
 (C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH  
 (D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH
- Q.9 A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of:  
 (A) 3 (B) 4 (C) 3000 (D) 10000
- Q.10 The first and second dissociation constants of an acid  $\text{H}_2\text{A}$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be:  
 (A)  $5.0 \times 10^{-5}$  (B)  $5.0 \times 10^{15}$  (C)  $5.0 \times 10^{-15}$  (D)  $0.2 \times 10^5$
- Q.11 An aqueous solution contains 0.01 M  $\text{RNH}_2$  ( $K_b = 2 \times 10^{-6}$ ) &  $10^{-4}$  M NaOH. The concentration of  $\text{OH}^-$  is nearly:  
 (A)  $2.414 \times 10^{-4}$  (B)  $10^{-4}$  M (C)  $1.414 \times 10^{-4}$  (D)  $2 \times 10^{-4}$
- Q.12 The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be  
 (A) 100% (B) 50% (C) 25% (D) 10%



- Q.13 What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is  $1.3 \times 10^{-9}$  and  $K_w = 1.0 \times 10^{-14}$   
 (A) 2.48 (B) 5.26 (C) 8.2 (D) 9.6
- Q.14 An aqueous solution contains 0.10 M  $H_2S$  and 0.20 M HCl. If the equilibrium constants for the formation of  $HS^-$  from  $H_2S$  is  $1.0 \times 10^{-7}$  and that of  $S^{2-}$  from  $HS^-$  ions is  $1.2 \times 10^{-13}$  then the concentration of  $S^{2-}$  ions in aqueous solution is  
 (A)  $5 \times 10^{-19}$  (B)  $5 \times 10^{-8}$  (C)  $3 \times 10^{-20}$  (D)  $6 \times 10^{-21}$
- Q.15 The pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is  
 (A) 1 (B) 6 (C) 7 (D) 9
- Q.16 If equilibrium constant of  
 $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$   
 is  $1.8 \times 10^{-5}$ , equilibrium constant for  
 $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$  is  
 (A)  $1.8 \times 10^{-9}$  (B)  $1.8 \times 10^9$  (C)  $5.55 \times 10^{-9}$  (D)  $5.55 \times 10^{10}$
- Q.17 The  $pK_a$  of a weak acid, HA, is 4.80. The  $pK_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be :  
 (A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22
- Q.18 If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [ $K_a = 2 \times 10^{-4}$ ], the pOH of the resulting solution is  
 (A) 3.4 (B) 3.7 (C) 7 (D) 10.3
- Q.19 An acid-base indicator which is a weak acid has a  $pK_a$  value = 5.45. At what concentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms ? [ $pK_a$  of acetic acid = 4.75]  
 (A) 4 : 1 (B) 6 : 1 (C) 5 : 1 (D) 3 : 1
- Q.20 The  $pK_a$  of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is :  
 (A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0
- Q.21 The solubility of  $A_2X_3$  is  $y \text{ mol dm}^{-3}$ . Its solubility product is  
 (A)  $6y^2$  (B)  $64y^4$  (C)  $36y^5$  (D)  $108y^5$
- Q.22 If  $K_{sp}$  for  $HgSO_4$  is  $6.4 \times 10^{-5}$ , then solubility of this substance in mole per  $m^3$  is  
 (A)  $8 \times 10^{-3}$  (B)  $6.4 \times 10^{-5}$  (C)  $8 \times 10^{-6}$  (D) None of these
- Q.23 The solubility of a sparingly soluble salt  $AB_2$  in water is  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ . Its solubility product is:  
 (A)  $10^{-15}$  (B)  $10^{-10}$  (C)  $4 \times 10^{-15}$  (D)  $4 \times 10^{-10}$
- Q.24 Which of the following is most soluble in water?  
 (A) MnS ( $K_{sp} = 8 \times 10^{-37}$ ) (B) ZnS ( $K_{sp} = 7 \times 10^{-16}$ )  
 (C)  $Bi_2S_3$  ( $K_{sp} = 1 \times 10^{-72}$ ) (D)  $Ag_3(PO_4)$  ( $K_{sp} = 1.8 \times 10^{-18}$ )

- Q.25 When equal volumes of the following solutions are mixed, precipitation of  $\text{AgCl}$  ( $K_{\text{sp}} = 1.8 \times 10^{-10}$ ) will occur only with:  
 (A)  $10^{-4} \text{ M } (\text{Ag}^+)$  and  $10^{-4} \text{ M } (\text{Cl}^-)$  (B)  $10^{-5} \text{ M } (\text{Ag}^+)$  and  $10^{-5} \text{ M } (\text{Cl}^-)$   
 (C)  $10^{-6} \text{ M } (\text{Ag}^+)$  and  $10^{-6} \text{ M } (\text{Cl}^-)$  (D)  $10^{-10} \text{ M } (\text{Ag}^+)$  and  $10^{-10} \text{ M } (\text{Cl}^-)$
- Q.26 The precipitate of  $\text{CaF}_2$  ( $K_{\text{sp}} = 1.7 \times 10^{-10}$ ) is obtained when equal volumes of the following are mixed  
 (A)  $10^{-4} \text{ M } \text{Ca}^{2+} + 10^{-4} \text{ M } \text{F}^-$  (B)  $10^{-2} \text{ M } \text{Ca}^{2+} + 10^{-3} \text{ M } \text{F}^-$   
 (C)  $10^{-5} \text{ M } \text{Ca}^{2+} + 10^{-3} \text{ M } \text{F}^-$  (D)  $10^{-3} \text{ M } \text{Ca}^{2+} + 10^{-5} \text{ M } \text{F}^-$
- Q.27 50 litre of a solution containing  $10^{-5}$  mole of  $\text{AgNO}_3$  is mixed with 50 litre of a  $2 \times 10^{-7} \text{ M}$   $\text{HBr}$  solution.  $[\text{Ag}^+]$  in resultant solution is : [Given :  $K_{\text{sp}} (\text{AgBr}) = 5 \times 10^{-13}$ ]  
 (A)  $10^{-5} \text{ M}$  (B)  $10^{-6} \text{ M}$  (C)  $10^{-7} \text{ M}$  (D) None of these
- Q.28 Solid  $\text{Ba}(\text{NO}_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4} \text{ M}$   $\text{Na}_2\text{CO}_3$  solution. At what concentration of  $\text{Ba}^{2+}$  will a precipitate begin to form ? ( $K_{\text{sp}}$  for  $\text{BaCO}_3 = 5.1 \times 10^{-9}$ )  
 (A)  $4.1 \times 10^{-5} \text{ M}$  (B)  $5.1 \times 10^{-5} \text{ M}$  (C)  $8.1 \times 10^{-8} \text{ M}$  (D)  $8.1 \times 10^{-7} \text{ M}$
- Q.29  $K_{\text{sp}}$  of  $\text{MX}_4$  and solubility of  $\text{MX}_4$  is  $S$  mol/litre is related by :  
 (A)  $S = [K_{\text{SP}}/256]^{1/5}$  (B)  $S = [128 K_{\text{SP}}]^{1/4}$  (C)  $S = [256 K_{\text{SP}}]^{1/5}$  (D)  $S = [K_{\text{SP}}/128]^{1/4}$
- Q.30 The pH of 0.1 M solution of the following salts increases in the order  
 (A)  $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$  (B)  $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$   
 (C)  $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$  (D)  $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
- Q.31 The range of most suitable indicator which should be used for titration of  $\text{X}^- \text{Na}^+$  (0.1 M, 10 ml) with 0.1 M  $\text{HCl}$  should be (Given:  $k_{\text{b}}(\text{X}^-) = 10^{-6}$ )  
 (A) 2 – 3 (B) 3 – 5 (C) 6 – 8 (D) 8 – 10
- Q.32 For sparingly soluble salt  $\text{ApBq}$ , the relationship of its solubility product ( $L_s$ ) with its solubility ( $S$ ) is  
 (A)  $L_s = S^{p+q}, p^p, q^q$  (B)  $L_s = S^{p+q}, p^p, q^p$  (C)  $L_s = S^{pq}, p^p, q^q$  (D)  $L_s = S^{pq}, (p.q)^{p+q}$
- Q.33 A solution which is  $10^{-3} \text{ M}$  each in  $\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  is treated with  $10^{-16} \text{ M}$  sulphide ion. If  $K_{\text{sp}}$ ,  $\text{MnS}, \text{FeS}, \text{ZnS}$  and  $\text{HgS}$  are  $10^{-15}, 10^{-23}, 10^{-20}$  and  $10^{-54}$  respectively, which one will precipitate first?  
 (A)  $\text{FeS}$  (B)  $\text{MnS}$  (C)  $\text{HgS}$  (D)  $\text{ZnS}$

**More than one may be correct**

- Q.34 Which of the following statement(s) is/are correct ?  
 (A) the pH of  $1.0 \times 10^{-8} \text{ M}$  solution of  $\text{HCl}$  is 8  
 (B) the conjugate base of  $\text{H}_2\text{PO}_4^-$  is  $\text{HPO}_4^{2-}$   
 (C) autoprotolysis constant of water increases with temperature  
 (D) when a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralization point  $\text{pH} = (1/2) \text{pK}_a$ .
- Q.35 Which of the following is true for alkaline aqueous solution?  
 (A)  $\text{pH} > \frac{\text{pK}_w}{2}$  (B)  $\text{pH} > \text{pOH}$  (C)  $\text{pOH} < \frac{\text{pK}_w}{2}$  (D)  $\text{pH} < \text{pOH}$

- Q.36 A buffer solution can be prepared from a mixture of  
 (A) sodium acetate and acetic acid in water  
 (B) sodium acetate and hydrochloric acid in water  
 (C) ammonia and ammonium chloride in water  
 (D) ammonia and sodium hydroxide in water.

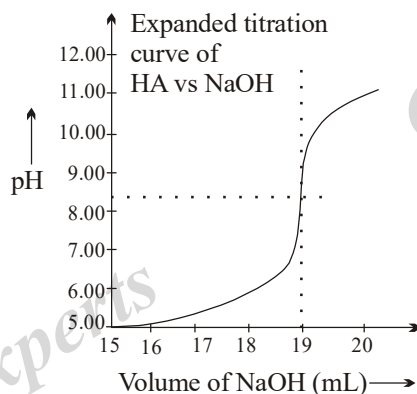
**Assertion & Reasoning type questions**

- Q.37 **Statement-1** : pH of  $10^{-7}$  M NaOH solution exists between 7 to 7.3 at  $25^\circ\text{C}$ .  
**Statement-2** : Due to common ion effect ionization of water is reduced.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- Q.38 **Statement-1** : Moles of  $\text{Sr}^{2+}$  furnished by sparingly soluble substance  $\text{Sr}(\text{OH})_2$  decreases due to dilution in its saturated solution.  
**Statement-2** : Solubility product constant of  $\text{Sr}(\text{OH})_2$  is not affected by dilution.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**Comprehension**

**Paragraph for Question Nos. 39 to 41**

1.2 g of a monoprotic acid HA, is titrated with 0.222 M NaOH solution. The pH of the solution is monitored with pH meter. A portion of the titration curve is shown in the diagram.



- Q.39 How many mL of NaOH is required to bring about the titration to its equivalence point ?  
 (A) 4.00 (B) 9.00 (C) 19.00 (D) None of these
- Q.40 What is the pH of solution at the equivalence point ?  
 (A) 3.50 (B) 7.00 (C) 8.40 (D) 5.00
- Q.41 What is the molar mass of HA ?  
 (A) 180 (B) 222 (C) 284 (D) None of these

## Match the column

Q.42

Column I

 Column II  
(At 25°C)

- |                                                                                                                                                                                                                                                         |                     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|
| (A) $\left( \begin{array}{l} 10 \text{ litre of } 0.03 \text{ N } X(OH)_2 \text{ (strong diacidic base)} \\ + \\ 5 \text{ litre of } 0.08 \text{ M } HNO_3 \\ + \\ 485 \text{ litre of } 0.01 \text{ M } NaNO_3 \end{array} \right)$                    | (P) $pH \simeq 3.7$ |
| (B) $\left( \begin{array}{l} 10 \text{ ml of } 0.5 \text{ M } RNH_3Cl \text{ (} K_h = 10^{-9} \text{)} \\ + \\ 40 \text{ ml of } 0.125 \text{ M } KOH \end{array} \right)$                                                                              | (Q) $pH \simeq 11$  |
| (C) $\left( \begin{array}{l} 100 \text{ ml of } 0.8 \text{ M } HCO_3^- \\ + \\ 100 \text{ ml of } 0.4 \text{ M } CO_3^{2-} \\ \text{(for } H_2CO_3, \text{ use } K_{a1} = 4 \times 10^{-7} \text{ \& } K_{a2} = 4 \times 10^{-11}) \end{array} \right)$ | (R) $pH \simeq 7$   |
| (D) Saturated aqueous solution of $Co(OH)_3$ ( $K_{sp} = 2.7 \times 10^{-43}$ )                                                                                                                                                                         | (S) $pH \simeq 10$  |

**ANSWER KEY****EXERCISE-1**

- Q.1  $6.022 \times 10^7$  Q.2  $0.6 \times 10^{-7}$   
 Q.3 (i) 6.51 ; (ii) (a) Basic, (b) Acidic Q.4 6.81  
 Q.5 (a) +1, (b) 2.87, (c) 11.13 (d) 6.97, (e) 7, (f) 6.97, (g) 11.30 (h) 9, (i) 3, (j)  $[H^+] = 6.18 \times 10^{-8}$ ; pH = 7.209  
 Q.6 (a)  $K_a = 10^{-8}$ , (b)  $K_b = 10^{-6}$  Q.7 1 0  
 Q.8 170.4 Q.9  $2.31 \times 10^{-8}$  M  
 Q.10 10.01 M Q.11  $1.11 \times 10^{-4}$   
 Q.12 4.87 Q.13  $V = 2.77 \times 10^4$  litre  
 Q.14 (a) 1, (b) 2.61  
 Q.15  $[H^+] = 1.612 \times 10^{-2}$  M,  $[CHCl_2COO^-] = 6.126 \times 10^{-3}$  M  
 Q.16  $[H^+] = 10^{-3}$  M,  $[CH_3COO^-] = 3.6 \times 10^{-4}$  M,  $[C_7H_5O_2^-] = 6.4 \times 10^{-4}$  M  
 Q.17 0.027 M, 0.073 M, 0.027 M,  $10^{-5}$  M Q.18 0.2091 M, 0.1909 M, 0.0091 M, 0  
 Q.19  $[OH^-] = 6.664 \times 10^{-6}$  Q.20 pH = 5  
 Q.21  $K_b = 6.25 \times 10^{-10}$  Q.22 0.56%, pH = 7  
 Q.23 pH = 10.42 Q.24 1.667%  
 Q.25 4.0% Q.26 (a) 6, (b)  $1 \times 10^{-5}$   
 Q.27 9 Q.28  $[OH^-] = 9.0 \times 10^{-6}$   
 Q.29 4.74 Q.30 0.05 mol  
 Q.31 9.56  
 Q.32 (a) pH = 9.239 (b) lowered (c) pH = 4.699  
 Q.33 8.7782 Q.34 9.7324  
 Q.35 85.71 % Q.36 pH = 7.3  
 Q.37 4.98  
 Q.38 (i) 2.85, (ii) 4.0969, (iii) 4.5229, (iv) 4.699, (v) 5.301, (vi) 8.699  
 Q.39  $K_b = 1.8 \times 10^{-5}$ , 5.27 Q.40 8.73  
 Q.41 pH = 11.3010 Q.42 (a) 0.0175%, pH = 1, (b) 4.757  
 Q.43  $QX_2$  is more soluble Q.44  $1.6 \times 10^{-8}$   
 Q.45  $[Cu^+] = 5 \times 10^{-11}$  M Q.46  $3.4 \times 10^{-11}$   
 Q.47  $2.6 \times 10^{-16}$  Q.48  $1.0 \times 10^{-18}$  M  
 Q.49  $1.0 \times 10^{-5}$  mol/lit Q.50  $5 \times 10^{-10}$  M  
 Q.51 12 mg  
 Q.52 (a) no precipitation will occur, (b) a precipitate will form  
 Q.53  $s = 1.203 \times 10^{-7}$  M  
 Q.54  $4 \times 10^{-7}$  mol/L AgBr,  $9 \times 10^{-7}$  mol/L AgSCN  
 Q.55  $[F^-] = 3 \times 10^{-3}$  M Q.56  $K_d = 1/K_f = 4.8 \times 10^{-4}$   
 Q.57  $2.8 \times 10^{-3}$  M

**EXERCISE-2**

- |                                 |        |        |        |        |         |          |
|---------------------------------|--------|--------|--------|--------|---------|----------|
| Q.1 A                           | Q.2 C  | Q.3 C  | Q.4 B  | Q.5 B  | Q.6 C   | Q.7 B    |
| Q.8 D                           | Q.9 D  | Q.10 C | Q.11 D | Q.12 B | Q.13 A  | Q.14 C   |
| Q.15 B                          | Q.16 B | Q.17 C | Q.18 D | Q.19 C | Q.20 C  | Q.21 D   |
| Q.22 D                          | Q.23 C | Q.24 D | Q.25 A | Q.26 B | Q.27 C  | Q.28 B   |
| Q.29 A                          | Q.30 B | Q.31 B | Q.32 A | Q.33 C | Q.34 BC | Q.35 ABC |
| Q.36 ABC                        | Q.37 A | Q.38 D | Q.39 C | Q.40 C | Q.41 C  |          |
| Q.42 (A) P, (B) Q, (C) S, (D) R |        |        |        |        |         |          |

## EXERCISE-1 (Subjective Questions)

First Law of Thermodynamics

Q.1 Predict sign of work done in following reactions at constant pressure.

|       | <i>Initial state</i>  |   | <i>Final state</i>            |
|-------|-----------------------|---|-------------------------------|
| (i)   | H <sub>2</sub> O (g)  | → | H <sub>2</sub> O (l)          |
| (ii)  | H <sub>2</sub> O (s)  | → | H <sub>2</sub> O (g)          |
| (iii) | H <sub>2</sub> O (l)  | → | H <sub>2</sub> O (s)          |
| (iv)  | CaCO <sub>3</sub> (s) | → | CaO (s) + CO <sub>2</sub> (g) |

Q.2 Calculate internal energy change for each of the following :

(a) 100 J of work is required to compress a gas and at the same time gas releases 20 J of heat.

(b) A piston is compressed from a volume of 8.3 L to 2.8 L against a constant pressure of 2 bar in the process heat gained by system is 350 J.

(c) A piston expands against 1 atm of pressure from 11.2 L to 29.2 L. In process 2820 J of heat is absorbed.

Q.3 Calculate magnitude of work done (**in kJ**) during vapourisation of 78 gm benzene (liquid) at its boiling point against 1 atm external pressure. Boiling point of benzene (liquid) = 360 K.

Q.4 Assume that 1 mol of an ideal gas is initially confined in a cylinder with a volume of 22.4 L at a temperature of 273 K. The external pressure is increased to  $1.5 \times 10^5$  Pa and the gas is compressed irreversibly and isothermally until  $P = 1.5 \times 10^5$  Pa. Find the value of work done (w).

[Given :  $R = 8.3$  J/mol-K,  $\ln 3 = 1.1$ ,  $\ln 2 = 0.7$ ]

Q.5 2 mole of an ideal gas undergoes isothermal compression along three different paths

(i) reversible compression from  $P_i = 2$  bar and  $V_i = 4$  L to  $P_f = 20$  bar

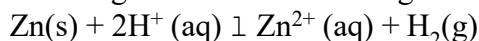
(ii) a single stage compression against a constant external pressure of 20 bar, and

(iii) a two stage compression consisting initially of compression against a constant external pressure of 10 bar until  $P_{\text{gas}} = P_{\text{ext}}$ , followed by compression against a constant pressure of 20 bar until  $P_{\text{gas}} = P_{\text{ext}}$ .

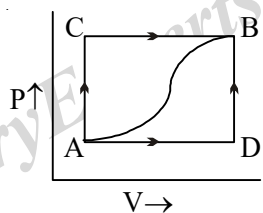
Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater? [Given :  $R = 0.08$  bar.L / mol.K]

Q.6 Lime is made commercially by decomposition of limestone, CaCO<sub>3</sub>. What is the change in internal energy when 1.00 mole of solid CaCO<sub>3</sub> ( $V = 34.2$  ml) absorbs 177.9 kJ of heat and decomposes at 25°C against a pressure of 1.0 atm to give solid CaO. (Volume = 16.9 ml) and CO<sub>2</sub> (g) ( $V = 24.4$  L).

Q.7 One mole of solid Zn is placed in excess of dilute H<sub>2</sub>SO<sub>4</sub> at 27 °C, in a cylinder fitted with a piston. Find the value of  $\Delta U$ ,  $q$  and  $w$  for the process if the area of piston is 500 cm<sup>2</sup> and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.



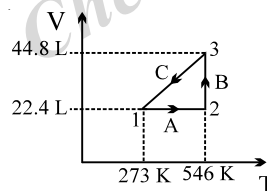
Q.8 Consider a mixture of air and gasoline vapour in a cylinder with a piston. The original volume is 40 cm<sup>3</sup>. If combustion of this mixture releases 950 J of energy, to what volume will the gas (**in L**) expands against a constant pressure of 5 bar if all the energy of combustion is converted into work to push back piston.

- Q.9 When a system is taken from state A to state B along the path ACB, 80J of heat flows into the system and the system does 30 J of work.
- (a) How much heat flows into the system along path ADB if the work done by the system is 10 J?
- (b) When the system is returned from state B to A along the curved path, the work done on the system is 20J. Does the system absorb or liberate heat, and how much?
- (c) If  $U_D - U_A = 40 \text{ J}$ , find the heat absorbed in the process AD and DB.
- 
- Q.10 A balloon filled with 40 mol of He has a volume of 876 L at  $0.08^\circ\text{C}$  and 1 atm pressure. At constant pressure the temperature of balloon is increased to  $38.08^\circ\text{C}$  causing the balloon to expand to a volume 998 L. Calculate q, w and  $\Delta U$  for the process in balloon.
- Q.11 When 3 mol  $\text{O}_2$  are heated at constant pressure of 3.25 atm. Its temperature is increased from 260K to 285 K. Given that molar heat capacity of  $\text{O}_2$  at constant pressure is  $29.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . Calculate q,  $\Delta H$ ,  $\Delta U$ .
- Q.12 If the given reaction is carried out with 1 mol  $\text{N}_2$  and excess of  $\text{H}_2$  at a constant pressure of 40 bar then volume contraction of 2 L is observed.  
 [Given :  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3$   $\Delta H^\circ = -90 \text{ kJ}$ ]  
 Now if 2 mol  $\text{N}_2$  and 8 mol  $\text{H}_2$  are taken then calculate  
 (a) PV work done  
 (b)  $\Delta U^\circ$  for given amount
- Q.13 Calculate q, w,  $\Delta H$  and  $\Delta U$  for process in which 88 gm of nitrous oxide gas  $\text{N}_2\text{O}$  is cooled from  $165^\circ\text{C}$  to  $55^\circ\text{C}$  at a constant pressure of 5 atm.  
 [For  $\text{N}_2\text{O}$   $C_v = 30.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $R = 8.3 \text{ J/mol-K}$ ]
- Q.14 Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a cont. ext. pressure of 1 atm. Calculate q, w,  $\Delta U$  &  $\Delta H$ . Calculate the corresponding value of all if the above process is carried out reversibly.
- Q.15 Calculate q, w,  $\Delta U$  and  $\Delta H$  (in Cal) when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at  $27^\circ\text{C}$ . (Given :  $\ln 5 = 1.6$ )
- Q.16 Methane (Considered to be an ideal gas) initially at  $27^\circ\text{C}$  and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by  $C_p = 20 + 0.001 T$  where  $C_p$  is in  $\text{J K}^{-1} \text{ mol}^{-1}$ . Calculate molar (a)  $\Delta H$  (b)  $\Delta U$ . [Given :  $R = 8 \text{ J/mol-K}$ ]
- Q.17 One mole of an ideal gas (not necessarily monoatomic) is subjected to the following sequence of steps.  
 (a) It is heated at constant volume from 298 K to 373 K  
 (b) It is expanded freely into a vacuum to double volume at 373 K.  
 (c) It is cooled reversibly at constant pressure to 298 K.  
 Calculate q, w,  $\Delta U$  and  $\Delta H$  for the overall process.

Q.18 One mole of a real gas is subjected to a isobaric process from (2 bar, 30 L, 300K) to (2 bar, 40 L, 500 K). The molar heat capacity of gas at constant volume and constant pressure are 25 J/K-mol and 40 J/K-mol respectively. What is the change in internal energy of the gas(in kJ) in this process?

Q.19 One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1,2 and 3. Fill in the blank space in the table given below assuming reversible steps.

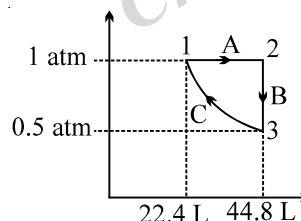
| State | P | V | T |
|-------|---|---|---|
| 1     |   |   |   |
| 2     |   |   |   |
| 3     |   |   |   |



| Step | Name of process | q | w | $\Delta E$ | $\Delta H$ |
|------|-----------------|---|---|------------|------------|
| A    |                 |   |   |            |            |
| B    |                 |   |   |            |            |
| C    |                 |   |   |            |            |

Q.20 One mole of an ideal monoatomic gas is put through reversible path as shown in figure. Fill in the blank in the table given below:

| State | P | V | T |
|-------|---|---|---|
| 1     |   |   |   |
| 2     |   |   |   |
| 3     |   |   |   |



| Step | Name of Process | q | w | $\Delta E$ | $\Delta H$ |
|------|-----------------|---|---|------------|------------|
| A    |                 |   |   |            |            |
| B    |                 |   |   |            |            |
| C    |                 |   |   |            |            |
|      | Cyclic          |   |   |            |            |

Q.21 One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

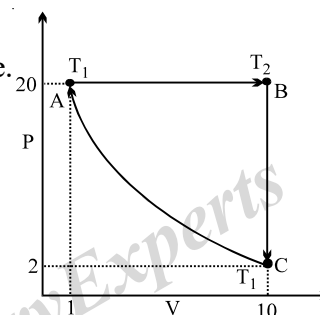
(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from  $T_1$  to  $T_2$ .

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

The steps are shown schematically in the figure shown.

(a) Calculate  $T_1$  and  $T_2$ .

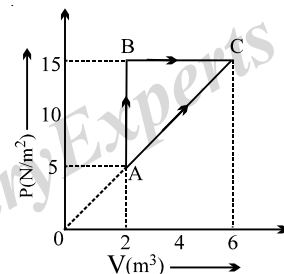
(b) Calculate  $\Delta U$ , q and w in calories, for each step and for the cycle.





Q.22 The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the:

- Path along which magnitude of work done is least.
- Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.
- Amount of heat supplied to the gas to go from A to B, if internal energy change of gas is 10 J.



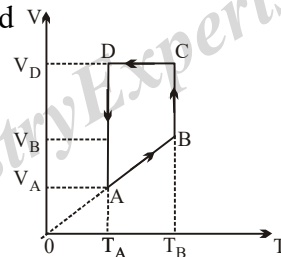
Q.23 Derive a mathematical expression for the work done on the surrounding when a gas that has the equation of state  $PV = nRT - \frac{n^2 a}{V}$  expands reversibly from  $V_i$  to  $V_f$  at constant temperature.

Q.24 A monoatomic ideal gas of two moles is taken through a reversible cyclic

process starting from A as shown in figure. The volume ratios are  $\frac{V_B}{V_A} = 2$  and

$\frac{V_D}{V_A} = 4$ . If the temperature  $T_A$  at A is  $27^\circ\text{C}$ , calculate:

- The temperature of the gas at point B.
- Heat absorbed or released by the gas in each process.
- The total work done by the gas during complete cycle.



### Relation between $\Delta H$ and $\Delta U$

Q.25 For the following reactions at constant pressure predict.

If  $\Delta H > \Delta U$ ,  $\Delta H < \Delta U$ ,  $\Delta H = \Delta U$ .

- $2\text{HF(g)} \rightarrow \text{H}_2\text{(g)} + \text{F}_2\text{(g)}$
- $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}$
- $4\text{NH}_3\text{(g)} + 5\text{O}_2\text{(g)} \rightarrow 4\text{NO(g)} + 6\text{H}_2\text{O(g)}$

Q.26 Calculate  $w$  and  $\Delta U$  when one mole of a liquid benzene is vaporised at its boiling point  $80^\circ\text{C}$  and 1 atm pressure.  $\Delta_{\text{vap}}H$  for the liquid is  $30.7 \text{ kJ/mol}$  at  $80^\circ\text{C}$ . [Given :  $R = 8.3 \text{ J/mol-K}$ ]

Q.27 Water expands when it freezes. Determine amount of work done in joules, when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

Q.28 What is  $\Delta U$  when 2.0 mole of liquid water vaporises at  $100^\circ\text{C}$ ? The heat of vaporisation,  $\Delta H_{\text{vap}}$  of water at  $100^\circ\text{C}$  is  $40.66 \text{ kJmol}^{-1}$ .

Q.29 If 1.0 kcal of heat is added to 1.2 L of  $\text{O}_2$  in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate  $\Delta U$  and  $\Delta H$  of the process.

Q.30 When 1 mole of ice melt at  $0^\circ\text{C}$  and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate  $\Delta H$  and  $\Delta U$  for the reaction.

Q.31 A certain mass of an ideal gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is  $50 \text{ J/}^\circ\text{C}$ . Calculate  $\Delta H$  (in kJ) of the process. (Given 1L atm = 100 J).

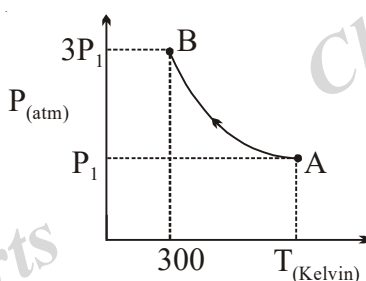
- Q.32 The molar enthalpy of vaporization of benzene at its boiling point (353 K) is  $30.84 \text{ kJ mol}^{-1}$ . What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point?
- Q.33 The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of  $\text{H}_2$  at 1.5 atm pressure is  $\Delta H = -0.31 \text{ KJ}$ . What is the  $\Delta U$ ?

**Adiabatic Expansion/ Compression**

- Q.34 Two mole of ideal diatomic gas ( $C_{V,m} = 5/2 R$ ) at 300 K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate  $q$ ,  $w$ ,  $\Delta H$  &  $\Delta U$ .
- Q.35 Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  (in kJ) by the system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas ( $\gamma = 4/3$ ) from 400K and pressure 10 atm to 1 atm. ( $R = 8.3 \text{ J/mol-K}$ )
- Q.36 1 mole of  $\text{CO}_2$  gas ( $\gamma = 4/3$ ) at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times. (a) What is the final temperature? (b) What is work done?
- Q.37 Three moles of a ideal gas at 200 K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas  $C_V$  is  $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$  in this temperature range. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and final  $V$  and final  $P$ . Given  $\left(\frac{5}{4}\right)^{0.3} = 2.1$ ,  $\left(\frac{5}{4}\right)^{\frac{13}{3}} = 2.61$ .

**Polytropic Process**

- Q.38 One mole of Argon is heated using  $PV^{5/2} = \text{constant}$ . By what amount heat is absorbed during the process, when temperature changes by  $\Delta T = 26 \text{ K}$
- Q.39 1 moles of an ideal diatomic gas is subjected to a process AB such that  $PT$  remains constant as shown. Calculate the magnitude of heat exchange during the process AB (in Cal).



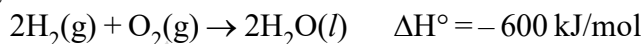
**Carnot Cycle**

- Q.40 A heat engine absorbs 760 kJ heat from a source at 380K. It rejects (i) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280 K. State which of these represent a reversible, an irreversible and an impossible cycle.
- Q.41 The efficiency of a carnot cycle is  $1/6$ . On decreasing the temperature of the sink by  $65^\circ\text{C}$ , the efficiency increases to  $1/3$ . Calculate the temperature of source and sink.
- Q.42 A carnot cycle has an efficiency of 40%. Its low temperature reservoir is at  $7^\circ\text{C}$ . What is the temperature of source?

Entropy Calculations

- Q.43 Indicate whether each process produces an increase or decrease in entropy of system  
 (a)  $\text{CO}_2(l) \rightarrow \text{CO}_2(g)$  (b)  $\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{NH}_4\text{Cl}(s)$   
 (c)  $\text{HCl}(s) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{Cl}(s)$  (d)  $2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$
- Q.44 The molar entropy of  $\text{He}(g)$  at  $27^\circ\text{C}$  and 1 atm is  $126 \text{ J K}^{-1} \text{ mol}^{-1}$ . Assuming ideal behaviour, calculate entropy of following.  
 [Given :  $R = 0.08 \text{ atm-L/mol-K}$ ,  $R = 8.3 \text{ J/mol-K}$ ,  $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ,  $\ln 10 = 2.3$ ]  
 (a) 0.1 mol of  $\text{He}(g)$  at  $27^\circ\text{C}$  and a volume of 4 litre.  
 (b) 0.3 mol of  $\text{He}(g)$  at  $27^\circ\text{C}$  and a volume of 2400 litre.
- Q.45 Which state in each of the following pairs has the higher entropy per mol of substance?  
 (a) Ice at  $-40^\circ\text{C}$  or ice at  $0^\circ\text{C}$   
 (b)  $\text{N}_2$  at STP or  $\text{N}_2$  at  $0^\circ\text{C}$  and 10 atm  
 (c) Water vapour at  $150^\circ$  and 1 atm or water vapour at  $100^\circ\text{C}$  and 2 atm.
- Q.46 A sample of 2 mol of a monoatomic ideal gas is expanded and heated. Its initial temperature is 300 K and its final temperature is 400 K. Its initial volume is 20 L and its final volume is 40L. Calculate  $\Delta S$ .
- Q.47 One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of  $\Delta S_{\text{gas}}$  and  $\Delta S_{\text{total}}$  under the following conditions.  
 (i) Expansion is carried out reversibly.  
 (ii) Expansion is carried out irreversibly where 836.8J of heat is less absorbed than in (i)  
 (iii) Expansion is free.
- Q.48 10 g of neon initially at a pressure of 506.625 kPa and temperature of 500 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.  
 [Given :  $\ln 380 = 3.64$ ,  $\ln 500 = 3.91$ ,  $\ln 5 = 1.6$ ,  $\ln 2 = 0.7$ ,  $R = 8.3 \text{ J/mol-K}$ ]  
 (i) Expansion is carried out reversibly.  
 (ii) Expansion occurs against a constant external pressure of 202.65 kPa.  
 (iii) Expansion is a free expansion.
- Q.49 One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{total}}$  in  
 (i) when the process carried out reversibly  
 (ii) when the process carried out irreversibly (one step)
- Q.50 For vaporisation of Benzene  $\Delta_{\text{vap}} H^\circ = 30.67 \text{ kJ/mol}$  and  $\Delta S_{\text{vap}}^\circ = 87 \text{ J K}^{-1} \text{ mol}^{-1}$ . Calculate  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{Total}}$  at  
 (a)  $70^\circ\text{C}$ ,  
 (b)  $79.5^\circ\text{C}$ ,  
 (c)  $90^\circ\text{C}$   
 (d) Calculate standard boiling point of benzene.  
 Comment about spontaneity of vaporisation of Benzene at these temperatures.  
 [Assume  $\Delta H$  to be temperature independent ]

Q.51 Consider the following reaction at 300 K



Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{total}}$ .

**Given :**  $[S_m^\circ(\text{H}_2) = 131 \text{ JK}^{-1} \text{ mol}^{-1}, S_m^\circ(\text{H}_2\text{O}(\text{l})) = 70 \text{ JK}^{-1} \text{ mol}^{-1}, S_m^\circ(\text{O}_2(\text{g})) = 205 \text{ JK}^{-1} \text{ mol}^{-1}]$

Q.52 Calculate change in entropy that occur when a sample containing 2 mol of water is heated from 50°C to 200°C at 1 atm pressure.  $[\ln 323 = 5.8, \ln 373 = 6.0, \ln 473 = 6.2]$

**[Given :**  $C_{p,m}(\text{H}_2\text{O}(\text{l})) = 75 \text{ J K}^{-1} \text{ mol}^{-1}$

$C_{p,m}(\text{H}_2\text{O}(\text{g})) = 35 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta_{\text{vap}}H_p(\text{H}_2\text{O}(\text{l})) = 37.3 \text{ kJ K}^{-1} \text{ mol}^{-1}$  at 100°C]

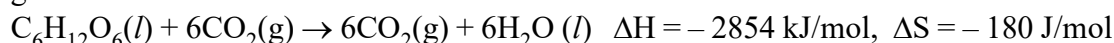
Q.53 Find  $\Delta H$ ,  $\Delta S$  and  $q$  for reversible heating of 0.5 mol of benzene from 25°C to 100°C at constant pressure of 1 atm. The normal boiling point of Benzene is 80°C and enthalpy change of vaporisation is

30.8 kJ/mol. **[Take:**  $\ln \frac{353}{298} = 0.17, \ln \frac{373}{353} = 0.05, C_{p,m} \text{ Benzene}(\text{g}) = 82 \text{ J/mol-K},$

$C_{p,m} \text{ Benzene}(\text{l}) = 136 \text{ J/mol-K}]$

### Free energy calculations and Third Law of Thermodynamics

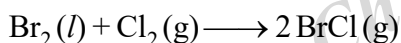
Q.54 How much energy is available for sustaining muscular and nervous activity from combustion of 1 mol of glucose molecules under standard conditions at 27°C.



Q.55 Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The entropy change is + 182.4 JK<sup>-1</sup> for the reaction as stated.

$$\Delta H_{\text{combustion [glucose]}} = -2808 \text{ KJ}$$

Q.56 Calculate the free energy change at 298 K for the reaction ;



For the reaction  $\Delta H^\circ = 29.3 \text{ kJ}$  & the entropies of  $\text{Br}_2(\text{l})$ ,  $\text{Cl}_2(\text{g})$  &  $\text{BrCl}(\text{g})$  at the 298 K are 152.3, 223.0, 239.7 J mol<sup>-1</sup> K<sup>-1</sup> respectively.

Q.57 (a) Calculate  $\Delta G$  (in J) for 1 mol of an ideal gas if it is isothermally pressurised from 1 atm to 3 atm at 27°C

(b) Calculate  $\Delta G$  if 1 mol of ice is pressurised at 0°C from 1 bar to 41 bar. Assume that ice has fixed volume. (Take :  $d_{\text{ice}} = 0.9 \text{ gm/ml}$ ) (1 bar L  $\approx$  100 J)

(c) Calculate  $\Delta G$  if 1 mol of liquid water is pressurised at 0°C from 1 bar to 51 bar. Assume that liquid water has fixed volume. ( $d_w = 1 \text{ gm/ml}$ )

(d) Calculate  $\Delta G$  if 1 mol of ice melts at 0°C and 50 bar.

(e) Calculate  $\Delta G$  if 1 mol of water is heated at constant pressure of 1 atm from 20°C to 80°C.

**[Take :**  $S_{\text{H}_2\text{O}(\text{l})} = 70 \text{ J mol}^{-1} \text{ K}^{-1}]$

- Q.58 5 mol  $\text{H}_2\text{O}(\ell)$  at 373 K and 1 atm is converted into  $\text{H}_2\text{O}(\text{g})$  at 373 K and 5 atm. Calculate  $\Delta G$  for this process. [Given :  $R = 2 \text{ Cal/K-mol}$ ]
- Q.59 The increase in Gibb's free energy (in kJ) of 19.5 gm of ethanol (density =  $0.78 \text{ gm cm}^{-3}$ ), when the pressure is increased isothermally from 1 bar to 3001 bar, is
- Q.60 The change in the Gibbs energy on heating of a substance from  $27^\circ\text{C}$  to  $127^\circ\text{C}$  at certain constant pressure was found to fit the expression :  $\Delta G(\text{J}) = -85.4 + 36.5 T(\text{K})$ . Calculate the value of  $\Delta S$  for the process.

- Q.61 Consider the following nine phase transformations.

- |                                                                                |                                                                |
|--------------------------------------------------------------------------------|----------------------------------------------------------------|
| (1) $\text{H}_2\text{O}(\text{s}, 1 \text{ atm}, 273 \text{ K}) \rightarrow$   | $\text{H}_2\text{O}(\ell, 1 \text{ atm}, 273 \text{ K})$       |
| (2) $\text{H}_2\text{O}(\text{s}, 1 \text{ atm}, 300 \text{ K}) \rightarrow$   | $\text{H}_2\text{O}(\ell, 1 \text{ atm}, 300 \text{ K})$       |
| (3) $\text{H}_2\text{O}(\text{s}, 1 \text{ atm}, 200 \text{ K}) \rightarrow$   | $\text{H}_2\text{O}(\ell, 1 \text{ atm}, 200 \text{ K})$       |
| (4) $\text{H}_2\text{O}(\text{s}, 0.5 \text{ atm}, 273 \text{ K}) \rightarrow$ | $\text{H}_2\text{O}(\ell, 0.5 \text{ atm}, 273 \text{ K})$     |
| (5) $\text{H}_2\text{O}(\text{s}, 2 \text{ atm}, 273 \text{ K}) \rightarrow$   | $\text{H}_2\text{O}(\ell, 2 \text{ atm}, 273 \text{ K})$       |
| (6) $\text{C}_6\text{H}_6(\ell, 1 \text{ atm}, 353 \text{ K}) \rightarrow$     | $\text{C}_6\text{H}_6(\text{g}, 1 \text{ atm}, 353 \text{ K})$ |
| (7) $\text{C}_6\text{H}_6(\ell, 1 \text{ atm}, 400 \text{ K}) \rightarrow$     | $\text{C}_6\text{H}_6(\text{g}, 1 \text{ atm}, 400 \text{ K})$ |
| (8) $\text{C}_6\text{H}_6(\ell, 1 \text{ atm}, 300 \text{ K}) \rightarrow$     | $\text{C}_6\text{H}_6(\text{g}, 1 \text{ atm}, 300 \text{ K})$ |
| (9) $\text{C}_6\text{H}_6(\ell, 2 \text{ atm}, 353 \text{ K}) \rightarrow$     | $\text{C}_6\text{H}_6(\text{g}, 2 \text{ atm}, 353 \text{ K})$ |

Given :  $T_{\text{nbP}}$  of  $\text{C}_6\text{H}_6(\ell) = 353 \text{ K}$

Predict the value (+ve, -ve, zero) of  $\Delta S$ ,  $\Delta H$ ,  $\Delta G$  and  $\Delta S_{\text{total}}$ .

- Q.62 The equilibrium constant of the reaction  $2\text{C}_3\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$  is found to fit the expression

$$\ln K_{\text{eq}} = -1.04 - \frac{1088}{T/\text{K}}$$

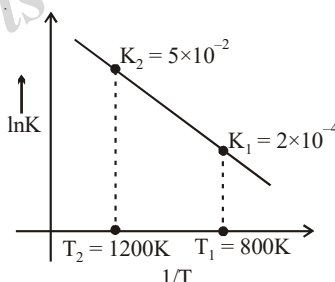
(where  $T/\text{K}$  is temperature expressed in Kelvin scale)

Calculate the standard reaction enthalpy and entropy at 400 K.

- Q.63 The value of  $K_p$  is  $1.1 \times 10^{-6}$  at 1000 K for synthesis of ammonia. Assuming value of  $\Delta H^\circ$  for this reaction is  $-0.83 \text{ kJ}$ . Calculate the value of  $K_p$  at 500K.  
[Given :  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $e^{0.1} = 1.1$ ]

- Q.64 For following equilibrium :  $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g})$

Variation of equilibrium constant with temperature is given as

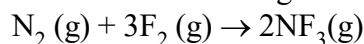


Assume  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature for given reaction.

[Given :  $\ln 2 = 0.7$ ,  $\ln 10 = 2.3$ ,  $R = 2 \text{ Cal / mol-Kelvin}$ ]

- (a) Calculate value of  $\Delta H^\circ$  (in KCal).  
(b) Calculate Value of  $\Delta G^\circ$  (in KCal) at 1200 K

Q.65 Consider the following reaction at 800 K



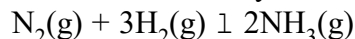
An equilibrium mixture contains the following partial pressure.

$$P_{\text{N}_2} = 0.2 \text{ atm}, P_{\text{F}_2} = 0.04 \text{ atm}, P_{\text{NF}_3} = 0.8 \text{ atm}$$

Calculate  $\Delta G^\circ$  and  $\Delta G$  at 800 K

[Given  $\log 5 = 0.7$ ,  $\ln 10 = 2.3$ ,  $R = 8.3 \text{ J/mol-K}$ ]

Q.66 Calculate  $\Delta G$  for ammonia synthesis at  $27^\circ\text{C}$  given following set of partial pressure.



$$\Delta G^\circ = -34.362 \text{ kJ}$$

Predict the direction in which reaction system will shift to reach equilibrium.

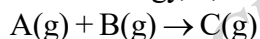
(a)  $P_{\text{N}_2} = 1 \text{ bar}, P_{\text{H}_2} = 0.01 \text{ bar}, P_{\text{NH}_3} = 1 \text{ bar}$

(b)  $P_{\text{N}_2} = 0.1 \text{ bar}, P_{\text{H}_2} = 0.1 \text{ bar}, P_{\text{NH}_3} = 1 \text{ bar}$

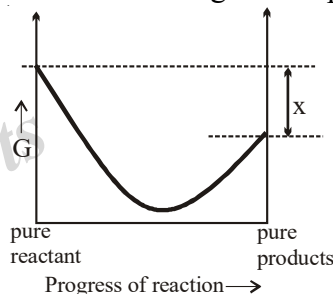
(c)  $P_{\text{N}_2} = 0.01 \text{ bar}, P_{\text{H}_2} = 0.01 \text{ bar}, P_{\text{NH}_3} = 1 \text{ bar}$

(d) Also comment on thermodynamics and kinetic feasibility of given reaction.

Q.67 The accompanying diagram shows how the free energy,  $G$ , Changes during a hypothetical reaction:



On the left are reactant each at 1 atm and on the right is the pure product also at 1 atm.



(a) What is the significance of minima in the plot

(b) What does quantity 'x', shows on the right side of diagram represents

(c) Why is the minimum in the plot on the right side of graph

## EXERCISE-2 (Objective Questions)

(I) *Mark the following statement as True or False.*

1. Pressure is an intensive property.
2. Like U and H, S is also a state function.
3. When a system undergoes a change at constant pressure, it is referred to an isothermal process.
4. A reversible process is always quasi-static.
5. The workdone by a gas during free expansion is equal to zero.
6. First law of T.D. is applicable to all processes irrespective to whether they are reversible or irreversible.
7. Entropy of universe is conserved.
8. Whenever a system undergoes a cyclic change

$$\oint \frac{dQ}{T} \leq 0$$

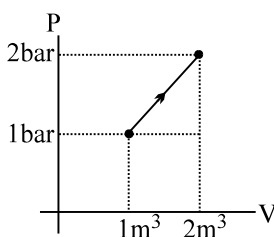
9. Positive value of  $\Delta S_{\text{system}}$  during the process can be taken as sole criterion of spontaneity.
10. A real crystal has higher entropy than the ideal crystal.

(II) *Fill in the blank with appropriate items:*

1. According to IUPAC conventions work done on the surroundings is \_\_\_\_\_.
2. A system is said to be \_\_\_\_\_ if it can neither exchange matter nor energy with surrounding.
3. A carnot cycle uses only \_\_\_\_\_ thermal reservoir.
4. A carnot cycle consists of only \_\_\_\_\_ processes.
5. The efficiency of a carnot engine can be increased by \_\_\_\_\_ sink temperature when the source temperature is held constant.
6. For a reversible adiabatic process,  $S = \text{constant}$  and hence it is called as an \_\_\_\_\_ process.
7. Entropy change of a system is determined by the \_\_\_\_\_ and \_\_\_\_\_ states only, irrespective of how the system has changed its states.
8. Solidification of liquid shows \_\_\_\_\_ in entropy.
9. When Fe(s) is dissolved in a aqueous HCl in a closed rigid vessel, the work done is \_\_\_\_\_.
10. For Non-spontaneous process at constant T & P,  $\Delta G$  is \_\_\_\_\_.

**(III) OBJECTIVE TYPE****Single correct :**

- Q.1 Out of boiling point (I), entropy (II), pH (III) and density (IV), Intensive properties are:  
 (A) I, II (B) I, II, III (C) I, III, IV (D) All of these
- Q.2 For which of the following processes  $|\Delta H| > |\Delta U|$   
 (A)  $2\text{HI(g)} \rightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ .  
 (B)  $\text{PCl}_5\text{(g)} \rightarrow \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$   
 (C) combustion of  $\text{CH}_4\text{(g)}$  at  $25^\circ\text{C}$   
 (D) both (B) and (C)
- Q.3 What is the change in internal energy when a gas contracts from 377 ml to 177 ml under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat?  
**[Take : (1 L atm) = 100 J]**  
 (A) -24 J (B) -84 J (C) -164 J (D) -248 J
- Q.4 Molar heat capacity of water in equilibrium with ice at constant pressure is  
 (A) zero (B)  $\infty$   
 (C)  $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$  (D)  $75.48 \text{ JK}^{-1} \text{ mol}^{-1}$
- Q.5 In which of the following changes work is done on the system, if all changes occur at constant pressure.  
 (A)  $2\text{O}_3\text{(g)} \longrightarrow 3\text{O}_2\text{(g)}$   
 (B)  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \longrightarrow 2\text{HI(g)}$   
 (C)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O(s)} \longrightarrow \text{MgSO}_4\text{(s)} + 7\text{H}_2\text{O(g)}$   
 (D)  $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \longrightarrow 2\text{NH}_3\text{(g)}$
- Q.6 A certain mass of a gas is expanded from [2 l, 20 atm, 300K] to [5 l, 10 atm, 320 K] against a constant external pressure of 5 atm. If heat capacity of the gas is  $100 \text{ J}^\circ\text{C}$  then enthalpy change of the process will be [1 atm litre = 100 J]  
 (A) 2 kJ (B) 0.5 kJ (C) 1.5 kJ (D) 1 kJ
- Q.7 An ideal gas initially at temperature  $T_1$  with  $\gamma = \frac{5}{3}$  expand adiabatically into vacuum to double its volume final temperature is given by :  
 (A)  $T_2 = T_1 (0.5)^{2/3}$  (B)  $T_2 = T_1$  (C)  $T_2 = T_1 2^{-1/3}$  (D)  $T_2 = \frac{T_1}{2}$
- Q.8 What is  $\Delta U$  for the process described by figure. Heat supplied during the process  $q = 100 \text{ kJ}$ .

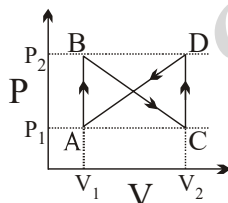


- (A) + 50 kJ (B) - 50 kJ (C) -150 kJ (D) + 150 kJ

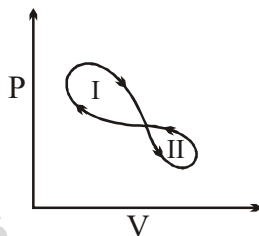


- Q.9 The heat capacity of liquid water is  $75.6 \text{ J/mol.K}$ , while the enthalpy of fusion of ice is  $6.0 \text{ kJ/mol}$ . What is the smallest number of ice cubes at  $0^\circ\text{C}$ , each containing  $9.0 \text{ g}$  of water, needed to cool  $500 \text{ g}$  of liquid water from  $20^\circ\text{C}$  to  $0^\circ\text{C}$ ?
- (A) 1 (B) 7 (C) 14 (D) None of these

- Q.10 An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :



- (A) zero (B) positive (C) negative (D) we cannot predict
- Q.11 A thermodynamic system undergoes a cyclic process, consists of two closed loops I and II. Then identify the **incorrect** statement(s)



- (A) Over one complete cycle net work done is negative.  
 (B) in loop I work done is positive.  
 (C) over one complete cycle sign of  $Q$  is positive  
 (D) in loop II heat flows out of the system.
- Q.12 The work done in adiabatic compression of 2 moles of ideal monoatomic gas against  $2 \text{ atm}$  external pressure if initially temperature and pressure is  $300 \text{ K}$  and  $1 \text{ atm}$ .
- (A)  $360 \text{ cal}$  (B)  $720 \text{ cal}$  (C)  $800 \text{ cal}$  (D)  $1000 \text{ cal}$
- Q.13 A diatomic ideal gas initially at  $273 \text{ K}$  is given  $100 \text{ cal}$  heat due to which system did  $209 \text{ J}$  work. Molar heat capacity ( $C_m$ ) of gas for the process is :
- (A)  $\frac{3}{2} R$  (B)  $\frac{5}{2} R$  (C)  $\frac{5}{4} R$  (D)  $5 R$
- Q.14 A gas ( $C_{v,m} = \frac{5}{2} R$ ) behaving ideally was allowed to expand reversibly and adiabatically from  $1 \text{ litre}$  to  $32 \text{ litre}$ . Its initial temperature was  $327^\circ\text{C}$ . The molar enthalpy change (in  $\text{J/mole}$ ) for the process is
- (A)  $-1125 R$  (B)  $-575 R$  (C)  $-1575 R$  (D) None of these
- Q.15 A non-ideal gas is subjected to an adiabatic process from  $(2\text{bar}, 10\text{L}, 300\text{K})$  to  $(5\text{bar}, 5\text{L}, 400\text{K})$  against a constant external pressure of  $5 \text{ bar}$ . Which of the following is **incorrect** regarding the gas?
- (A)  $q = 0$  (B)  $W = +2600\text{J}$  (C)  $\Delta U = +2500\text{J}$  (D)  $\Delta H = +3000\text{J}$

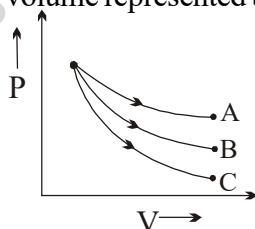
Q.16 Calculate heat capacity of 40 gm triatomic nonlinear gas ( $M = 20$  gm/mol). If it is subjected to a process such that pressure exerted is directly proportional to square of volume at under normal conditions.

- (A)  $\frac{10}{3} R$  (B)  $\frac{20}{3} R$  (C)  $\frac{17}{6} R$  (D)  $\frac{17}{3} R$

Q.17 A definite amount of an ideal gas ( $\gamma = 1.5$ ) undergoes a change of state in which heat exchange is equal to work done ( $q = w$ ). Molar heat capacity of the gas is :

- (A)  $2R$  (B)  $3R$  (C)  $R$  (D)  $\frac{3}{2} R$

Q.18 Three ideal gases Ne,  $\text{CO}_2$  and  $\text{CH}_4$  are subjected to reversible adiabatic expansion process from same initial state to same final volume represented by A, B & C. Which of the gas is  $\text{CH}_4$ ?



- (A) A (B) B (C) C (D) can't be determined

Q.19 One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.

State-1 (8.0 bar, 4.0 litre, 300 K)

State-2 (2.0 bar, 16 litre, 300 K)

State-3 (1.0 bar, 32 litre, 300 K)

Total heat absorbed by the gas in the process is :

- (A) 116 J (B) 40 J (C) 4000 J (D) None of these

Q.20 The maximum efficiency of a heat engine operating between  $100^\circ\text{C}$  and  $25^\circ\text{C}$  is

- (A) 20.11% (B) 22.2% (C) 25.17% (D) None

Q.21 A heat engine operating between  $227^\circ\text{C}$  and  $27^\circ\text{C}$  absorbs 2 Kcal of heat from the  $227^\circ\text{C}$  reservoir reversibly per cycle. The amount of work done in one cycle is

- (A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal

Q.22 Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change ( $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ ) for given process.

[Given :  $\ln 2 = 0.70$  and  $R = 8.0$  J/mol/K]

- (A) 56 J/K (B) 14 J/K (C) 16 J/K (D) None of these

Q.23 Two moles of ideal monoatomic gas was taken through isochoric heating from 100 K to 800 K. If the process is carried out irreversibly (one step) then  $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$  is

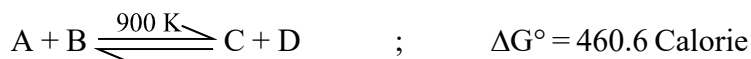
[Given :  $\ln 2 = 0.7$  and  $R = 2$  cal / mol. K]

- (A) 0 (B) 3.675 cal/K (C) 7.35 cal/K (D) None of these

- Q.24 What is Entropy change when volume of 2.8 gm of  $N_2$  changes from 4 litre to 2 litre at constant temperature of  $27^\circ C$  ?  
 $[\ln 2 = 0.7, R = 8.3 \text{ J/mole-K}]$   
 (A) 0.851 Joule (B) 0.581 Joule (C) -0.581 Joule (D) -0.851 Joule
- Q.25 If  $\Delta H_{\text{vaporisation}}$  of substance X (l) (molar mass : 30 g/mol) is 300 J/g at its boiling point 300 K, then molar entropy change for reversible condensation process is  
 (A) 30 J/mol.K (B) -300 J/mol.K (C) -30 J/mol.K (D) None of these
- Q.26 For a fixed amount of an ideal monoatomic gas  $\left(\gamma = \frac{5}{3}\right)$ , the **change in internal energy of gas**, when the pressure changes from 5 bar to 10 bar at constant volume of 10 L is  
 (A) 7500 J (B) -7500 J (C) 75 J (D) 5000 J
- Q.27 In the caves limestone is formed by following reaction.  
 $Ca^{2+}(aq) + 2CO_3^{2-}(aq) \longrightarrow CaCO_3(s) + CO_2(g) + H_2O(l)$   
 If 1 mol of  $CaCO_3$  is formed at 298 K and 1 atm pressure, the reaction performs 2.47 kJ of PV work, pushing back the atmosphere as the gaseous  $CO_2$  form. At the same time 38.95 kJ of heat is absorbed from environment. Identify the **correct** value.  
 (A)  $\Delta H = 38.95 \text{ kJ/mol}$  (C)  $\Delta U = 36.48 \text{ kJ/mol}$   
 (B)  $\Delta H - \Delta U = 2.47 \text{ kJ/mol}$  (D) All are correct
- Q.28 For a perfectly crystalline solid  $C_{p,m} = aT^2$  where 'a' is constant, if  $C_{p,m}$  is  $0.2 \text{ JK}^{-1}\text{mol}^{-1}$  at 10K, then molar entropy at 100 K is :  
 (A) 100 J/K-mol (B)  $3.3 \times 10^5 \text{ J/K-mol}$   
 (C) 10 kJ/K-mol (D) 10 J/K-mol
- Q.29 In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done the change in Gibbs free energy (dG) and change in entropy (dS) satisfy the criteria-  
 (A)  $(dS)_{V,E} = 0, (dG)_{T,P} = 0$  (B)  $(dS)_{V,E} = 0, (dG)_{T,P} > 0$   
 (C)  $(dS)_{V,E} < 0, (dG)_{T,P} < 0$  (D)  $(dS)_{V,E} > 0, (dG)_{T,P} < 0$
- Q.30 Which substance is expected to have highest molar entropy under standard conditions of temperature and pressure?  
 (A)  $NO_2(g)$  (B)  $N_2O_4(g)$  (C)  $I_2(s)$  (D)  $H_2O(l)$
- Q.31 For the reaction :  $NH_4CONH_2(s) \rightleftharpoons 2NH_3(g) + CO(g)$   
 If equilibrium pressure is x bar, then  $\Delta_r G^\circ$  would be :  
 (A)  $-3RT \left[ \ln x + \frac{2}{3} \ln 2 - \ln 3 \right]$  (B)  $-3RT [\ln x + 2 \ln 2 - \ln 3]$   
 (C)  $-RT [3 \ln x - 2 \ln 3]$  (D)  $-RT [3 \ln x]$

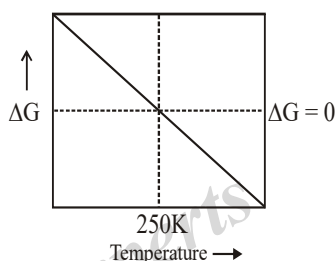
- Q.32 What is  $\Delta_r G$  (KJ/mole) for synthesis of ammonia at 298 K at following sets of partial pressure:  
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ;  $\Delta_r G^\circ = -33$  KJ/mole. [Take  $R = 8.3$  J/K mole,  $\log 2 = 0.3$ ;  $\log 3 = 0.48$ ]
- |                |       |       |        |
|----------------|-------|-------|--------|
| Gas            | $N_2$ | $H_2$ | $NH_3$ |
| Pressure (atm) | 1     | 3     | 0.02   |
- (A) + 6.5      (B) - 6.5      (C) + 60.5      (D) - 60.5

- Q.33 Calculate  $\log_{10} \{[C]_{eq}/[A]_{eq}\}$  where [C] and [A] are equilibrium molar concentration of respective species, when 2 mole each of A and B were allowed to come to equilibrium at 900 K.



Take :  $\ln X = 2.303 \log X$   
 $R = 2 \text{ Cal/K mole}$

- (A)  $-5.56 \times 10^{-02}$       (B)  $-5.57 \times 10^{-03}$   
 (C)  $-1.1 \times 10^{-2}$       (D)  $-1.1 \times 10^{-3}$
- Q.34 Diagram shows how  $\Delta G$  for a hypothetical reaction changes as temperature changes. Select **incorrect** statement among following.



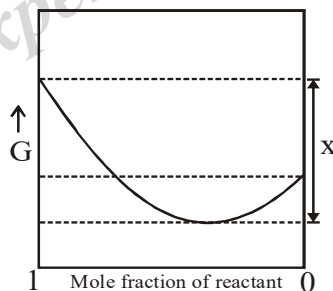
- (A)  $\Delta H > 0$       (B)  $\Delta S > 0$   
 (C) process is spontaneous, if  $T < 250\text{K}$   
 (D) system is in equilibrium at  $T = 250\text{K}$
- Q.35 For a hypothetical reaction :  $A(g) + B(g) \rightarrow C(g)$   
 Initially all reactants and products are at 1 atm.

**Statement-1 :** 'x' represent  $\Delta G^\circ$

**Statement-2 :** In this reaction all reactant would get converted into product.

**Statement-3 :** At equilibrium partial pressure of C will be greater than 1 atm.

**Statement-4 :** At equilibrium total pressure of mixture will be greater than 3 atm.

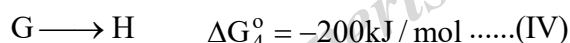
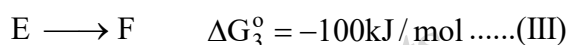
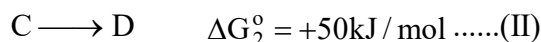
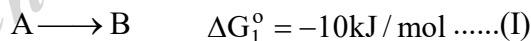


- (A) Only statement-1 & 4 are incorrect.      (B) Only statement-1 & 3 are correct.  
 (C) Only statement-2 & 3 are correct.      (D) Only Statement-3 is correct.

Q.36 Identify the **correct** statement -

- (A) Endothermic reaction are never spontaneous.
- (B) During spontaneous process Gibbs free energy will always decrease.
- (C) If  $\Delta_{\text{rxn}} G^\circ$  for a reaction is negative then equilibrium constant will be greater than one.
- (D) In spontaneous process  $\Delta S_{\text{surr}}$  always increases.

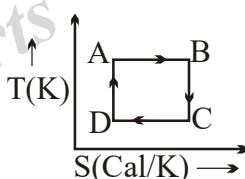
Q.37 For following equations.



Identify the correct statement(s):

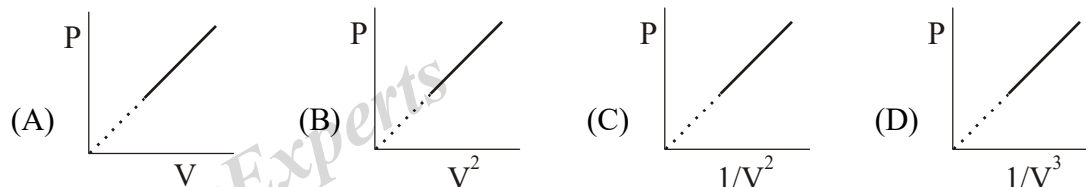
- (A) IV reaction will be fastest.
- (B) Only III reaction is spontaneous
- (C) IV reaction will have maximum extent.
- (D) Rate of reactions will be  $\text{IV} > \text{III} > \text{I} > \text{II}$

Q.38 A substance is subjected to a four step reversible process **ABCD** as shown. Identify the **correct** statements out of the following:

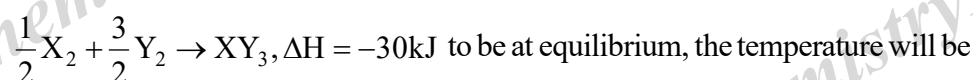


- (A) Step A-B is an exothermic step
- (B) Step B-C is an endothermic step
- (C) Step C-D is an exothermic step
- (D) Step D-A is an endothermic step

Q.39 For an ideal gas subjected to different processes as shown by the graphs, select the graph which will involve greatest amount of heat exchange if initial & final temperature are same in all.



Q.40 Standard entropy of  $X_2$ ,  $Y_2$  and  $XY_3$  are 60, 40 and 50  $\text{JK}^{-1}\text{mol}^{-1}$ , respectively. For the reaction,

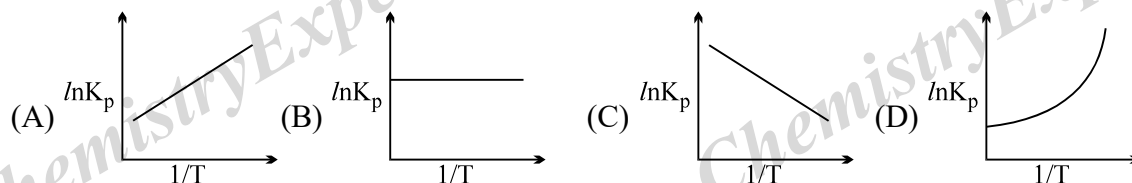


- (A) 1250 K
- (B) 500 K

(C) 750 K

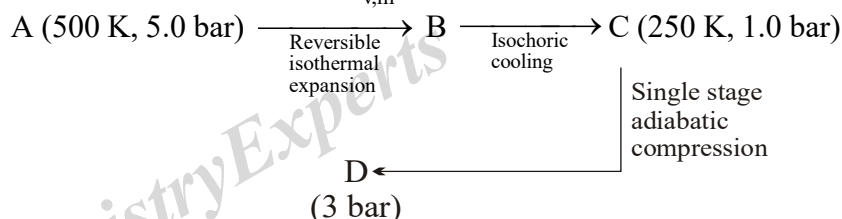
(D) 1000 K

Q.41 An exothermic reaction is represented by the graph :



**More than one correct:**

Q.42 Two moles of an ideal gas ( $C_{v,m} = 3/2R$ ) is subjected to following change of state.

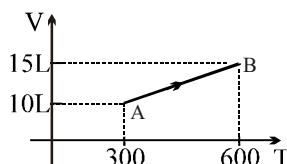


The correct statement is / are :

- (A) The pressure at B is 2.0 bar
- (B) The temperature at D is 450 K
- (C)  $\Delta H_{CD} = 1000 R$
- (D)  $\Delta U_{BC} = 375 R$

Q.43 If one mole monoatomic ideal gas was taken through process AB as shown in figure, then select correct option(s).

**Given :**  $\ln 1.5 = 0.4$



- (A)  $w_{AB} = -1496.52 J$
- (B)  $q_{AB} = 5237.82 J$
- (C)  $\Delta H_{AB} = 3741.3 J$
- (D)  $\Delta S_{AB}$  is +ve

Q.44 Which statement is / are correct:

- (A) Final temperature in reversible adiabatic expansion is lesser than in irreversible adiabatic expansion.
- (B) When heat is supplied to an ideal gas in an isothermal process, kinetic energy of gas will increase
- (C) When an ideal gas is subjected to adiabatic expansion it gets cooled
- (D) Entropy increases in atomisation of dihydrogen

Q.45 Identify the **correct** statement(s)

- (A) Spontaneous reactions are always fast
- (B) Reaction that is non-spontaneous in forward direction is always spontaneous in backward direction.

(C) During a reversible process always  $\Delta G = 0$ .

(D)  $\Delta H = Q_p$  only when there is no non PV work involved.

- Q.46 One mole of an ideal diatomic gas ( $C_v = 5 \text{ CalK}^{-1}\text{mol}^{-1}$ ) changes its state from **state 1** ( $27^\circ\text{C}$ , 1L) to **state 2** ( $127^\circ\text{C}$ , 10L). For this process, which of the statements is(are) **correct**?

(Given :  $R = 2 \text{ CalK}^{-1} \text{mol}^{-1}$ ).

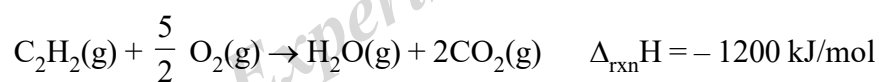
(A)  $\Delta H = 700 \text{ cal}$

(B)  $\Delta U = 500 \text{ cal}$

(C)  $\Delta S = 5\ln(4/3) + 2\ln 10 \text{ calK}^{-1}$

(D)  $\Delta G$  of the process can't be calculated using given information.

- Q.47 Following process is used in welding metals.



If 39 gm of acetylene undergo combustion at 1 atm and  $327^\circ\text{C}$ , then :

[Take :  $R = \frac{25}{3} \text{ JK}^{-1} \text{mol}^{-1}$ ]

(A)  $q_v$  for process =  $-1197.5 \text{ kJ}$

(B) Work done =  $2.5 \text{ kJ}$

(C)  $\Delta S_{\text{surr}} = 3000 \text{ J/K}$

(D)  $\Delta_{\text{rxn}}S$  is negative

- Q.48 In isothermal ideal gas compression:

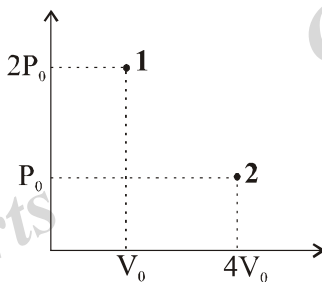
(A)  $w$  is +ve

(B)  $\Delta H$  is zero

(C)  $\Delta S_{\text{gas}}$  is +ve

(D)  $\Delta G$  is +ve

- Q.49 A liquid which is confined inside an adiabatic piston is suddenly taken from state (1) to state (2) by a single step process. If the piston comes to rest at point (2) as shown. Then choose the correct option(s):



(A)  $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$

(B)  $\Delta U = \frac{3P_0 V_0}{(\gamma - 1)}$

(C)  $\Delta H = -P_0 V_0$

(D)  $\Delta U = -3P_0 V_0$

- Q.50 The crystalline hydrate  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s})$  loses water when placed in large closed, dry vessel  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s}) \longrightarrow \text{Cd}(\text{NO}_3)_2(\text{s}) + 4\text{H}_2\text{O}(\text{g})$ . Then identify the correct statement(s):

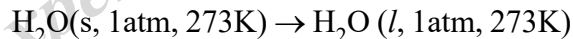
(A) Reaction is endothermic

(B) Reaction is exothermic

(C) Under mentioned conditions  $\Delta G_{\text{reaction}} < 0$

(D) Reaction is entropy driven.

Q.51 For process :



[Given : Normal freezing point of water is 273].

The **correct** set of thermodynamic parameters is/are :

(A)  $\Delta G = 0$ ,  $q > 0$ ,  $\Delta S_{\text{surr}} < 0$

(B)  $\Delta G < 0$ ,  $q > 0$ ,  $\Delta S_{\text{Total}} < 0$

(C)  $\Delta S_{\text{sys}} > 0$ ,  $\Delta S_{\text{surr}} < 0$ ,  $\Delta U > 0$

(D)  $\Delta G > 0$ ,  $q > 0$ ,  $\Delta S_{\text{surr}} < 0$

### Assertion Reason :

Q.52 **Statement -1** : There is no change in enthalpy of an ideal gas during compression at constant temperature.

**Statement -2** : Enthalpy of an ideal gas is a function of temperature and pressure.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

Q.53 **Statement-1** : Due to adiabatic expansion, temperature of an ideal gas always decreases.

**Statement-2** : For an adiabatic expansion  $\Delta U = w$

(A) Statement-1 is true, statement-2 is true; statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true; statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

Q.54 **Statement-1** : Entropy of an isolated system must increase in an irreversible adiabatic process.

**Statement-2** : Any process in an isolated system must be adiabatic process.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is **NOT** the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

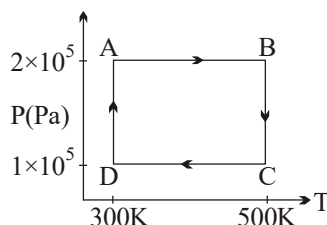
(D) Statement-1 is false, statement-2 is true.

### Comprehension :

#### **Paragraph Question no. 55 to 57**

Two moles of helium gas are taken over the cycle ABCDA, as shown in the P-T diagram.

[  $\ln 2 = 0.69$  ]



Q.55 Assuming the gas to be ideal the work done on the gas in taking it from A to B is –

(A) 200 R

(B) 300 R

(C) – 400 R

(D) 500 R



- Q.56 The work done on the gas in taking it from D to A is –  
 (A) – 414 R (B) + 414 R (C) – 690 R (D) + 690 R
- Q.57 The net work done on the gas in the cycle ABCDA is –  
 (A) Zero (B) – 276 R (C) 1076 R (D) 1904 R

**Match the column :**

- Q.58 Match Column – I with Column – II :

**Column – I (Ideal Gas)**

- (A) Reversible isothermal process  
 (B) Reversible adiabatic process  
 (C) Irreversible adiabatic process  
 (D) Irreversible isothermal process

**Column - II (Related equations)**

- (P)  $W = 2.303nRT \log (P_2/P_1)$   
 (Q)  $W = nC_{V_m} (T_2 - T_1)$   
 (R)  $W = -2.303nRT \log (V_2/V_1)$   
 (S)  $W = - \int_{V_i}^{V_f} P_{\text{ext.}} dV$

- Q.59 Match the column-I with column-II.

**Note that** column-I may have more than one matching options in column-II.**Column-I**

- (A) Reversible adiabatic compression  
 (B) Reversible vaporisation  
 (C) Adiabatic free expansion of ideal gas in vacuum at constant temperature  
 (D) Dissociation of  
 $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

**Column-II**

- (P)  $\Delta S_{\text{system}} > 0$   
 (Q)  $\Delta S_{\text{system}} < 0$   
 (R)  $\Delta S_{\text{surrounding}} < 0$   
 (S)  $\Delta S_{\text{surrounding}} = 0$

- Q.60

**Column I**

- (A) For the process  
 $A(l) \rightarrow A(s), \Delta H \text{ \& } \Delta V$  may be
- (B)  $A_2(\text{s}) + B_2(\text{g}) \rightleftharpoons C_2(\text{s}) + D_2(\text{s})$   
 $\Delta H \text{ \& } \Delta G$  may be
- (C) For the given reaction  
 $A_2(\text{g}) \rightleftharpoons B(\text{g}) + C(\text{g}),$   
 $E_{a(\text{forward})} = 50 \text{ kJ/mol}$   
 and  $E_{a(\text{backward})} = 40 \text{ kJ/mol},$   
 at very high temperature  $\Delta H \text{ \& } \Delta G$  are
- (D) For the given reaction  
 $A(\text{g}) \rightleftharpoons B(\text{g}),$  at very low temperature  
 $\Delta H \text{ \& } \Delta G$  may be

**Column II**

- (P) – ve, + ve  
 (Q) + ve, – ve  
 (R) + ve, + ve  
 (S) – ve, – ve

**ANSWER KEY****EXERCISE-1**

Q.1 (i) +ve, (ii) -ve, (iii) -ve, (iv) -ve      Q.2 (a) 80 J (b) 1.45 kJ (c) 996.6 J

Q.3 3      Q.4 1.13 kJ

Q.5 (i) 18.424 bar.L; (ii) 72 bar.L; (iii) 40 bar.L  
Magnitude of work is maximum in single stage compression

Q.6  $q = 177.9 \text{ kJ}$ ,  $w = -2.5 \text{ kJ}$ ;  $\Delta E = 175.4 \text{ kJ}$

Q.7  $\Delta E = -39.03 \text{ kJ/mole}$ ;  $q = -36.5 \text{ kJ}$ ;  $w = -2.53 \text{ kJ}$

Q.8 1.94 L      Q.9 (a) +60 J (b) -70 J (c) 50 J, +10 J,

Q.10  $q = 31.3 \text{ kJ}$ ,  $w = -12.35 \text{ kJ}$ ,  $\Delta U = 18.95 \text{ kJ}$

Q.11  $\Delta H = q = 2205 \text{ J}$ ,  $\Delta U = 1582.5 \text{ J}$

Q.12 (a) 16 kJ; (b) -164 kJ

Q.13  $q = \Delta H = -8.536 \text{ kJ}$ ,  $w = 1.826 \text{ kJ}$ ,  $\Delta U = -6.71 \text{ kJ}$

Q.14  $w_{\text{irr}} = -9353.25$ ,  $w_{\text{rev}} = -17288.47 \text{ J}$ ,  $\Delta U = \Delta H = 0$

Q.15  $w = -960 \text{ Cal}$ ,  $q = -W = 965.6 \text{ Cal}$ ,  $\Delta U = 0$ ,  $\Delta H = 0$

Q.16 (a)  $\Delta H = 6.135 \text{ kJ mol}^{-1}$ .      (b)  $\Delta U = 3.645 \text{ kJ mol}^{-1}$ .

Q.17  $\Delta U \text{ \& } \Delta H = 0$ ;  $w = 623.55$ ;  $q = -623.55 \text{ J mol}^{-1}$

Q.18 6 kJ

Table-1

| State | P     | V    | T   |
|-------|-------|------|-----|
| 1     | 1 atm | 22.4 | 273 |
| 2     | 2 atm | 22.4 | 546 |
| 3     | 1 atm | 44.8 | 546 |

Q.19

| Step | Name of process | q             | w              | $\Delta E$    | $\Delta H$    |
|------|-----------------|---------------|----------------|---------------|---------------|
| A    | Isochoric       | $3/2 R(273)$  | 0              | $3/2 R(273)$  | $5/2 R(273)$  |
| B    | Isothermal      | $546 R \ln 2$ | $-546 R \ln 2$ | 0             | 0             |
| C    | Isobaric        | $-5/2 R(273)$ | $R(273)$       | $-3/2 R(273)$ | $-5/2 R(273)$ |

Q.20

| State | P     | V    | T   |
|-------|-------|------|-----|
| 1     | 1 atm | 22.4 | 273 |
| 2     | 1     | 44.8 | 546 |
| 3     | 0.5   | 44.8 | 273 |

| Step | Name of process | q                      | w                       | $\Delta E$    | $\Delta H$    |
|------|-----------------|------------------------|-------------------------|---------------|---------------|
| A    | Isobaric        | $5/2 R(273)$           | $-R(273)$               | $3/2 R(273)$  | $5/2 R(273)$  |
| B    | Isochoric       | $-3/2 R(273)$          | 0                       | $-3/2 R(273)$ | $-5/2 R(273)$ |
| C    | Isothermal      | $-273 R \ln 2$         | $273 R \ln 2$           | 0             | 0             |
|      | Cyclic          | $R(273) - 273 R \ln 2$ | $-R(273) + 273 R \ln 2$ | 0             | 0             |

Q.21 (a)  $T_1 = 243.60 \text{ K}$ ;  $T_2 = 2436.0 \text{ K}$ , (b)  $\Delta U = 0$ ;  $q = -w = +3262.88 \text{ cal}$ 

Q.22 (a) AC, (b) 170 J, (c) 10 J

$$Q.23 \quad w = -nRT \ln \frac{V_f}{V_i} - n^2 a \left( \frac{1}{V_f} - \frac{1}{V_i} \right)$$

Q.24 (a) 600 K,  
 (b)  $q_{AB} = 3000 \text{ cal}$ ;  $q_{BC} = 1663 \text{ cal}$ ;  $q_{CD} = -1800 \text{ cal}$ ;  $q_{DA} = -1663 \text{ cal}$ ,  
 (c)  $w = -1200 \text{ cal}$

Q.25 (a)  $\Delta H = \Delta U$ , (b)  $\Delta H < \Delta U$  (c)  $\Delta H > \Delta U$ Q.26  $w = -2.93 \text{ kJ/mol}$ ,  $\Delta U = 27.77 \text{ kJ/mol}$  Q.27  $-10 \text{ J}$ Q.28  $\Delta E = 75.11 \text{ kJ}$  Q.29  $\Delta E = 0.993 \text{ kcal}$ ,  $\Delta H = 1 \text{ kcal}$ Q.30  $\Delta H \cong \Delta U = 1440 \text{ calories}$  Q.31  $15.7 \text{ kJ}$ Q.32  $\Delta U = 27.91 \text{ kJ mol}^{-1}$ ,  $t = 514 \text{ sec.}$  Q.33  $-0.3024 \text{ kJ}$ Q.34  $\Delta U = w = -1247.1$ ;  $\Delta H = -1745.94 \text{ J}$ Q.35  $q = 0$ ,  $w = -2.24 \text{ kJ}$ ,  $\Delta U = -2.241 \text{ kJ}$ ,  $\Delta H = -2.988 \text{ kJ}$ Q.36  $T_2 = 100 \text{ K}$ ;  $w = -5.016 \text{ kJ}$ Q.37  $q = 0$ ;  $w = \Delta U = 4.12 \text{ kJ}$ ;  $\Delta H = 5.37 \text{ kJ}$ ;  $V_f = 11.8 \text{ dm}^3$ ;  $P = 5.21 \text{ atm}$ Q.38  $180 \text{ J}$  Q.39  $5400$  Q.40 (i) irreversible, (ii) reversible, (iii) impossibleQ.41  $117^\circ\text{C}$ ,  $52^\circ\text{C}$  Q.42  $193.66^\circ\text{C}$ 

Q.43 (a) Entropy will increase  
 (b) Entropy will decrease  
 (c) Entropy will decrease  
 (d) Entropy will decrease

Q.44 (a)  $13.05 \text{ JK}^{-1}$ , (b)  $52.24 \text{ JK}^{-1}$

Q.45 (a) ice at  $0^\circ\text{C}$   
 (b)  $\text{N}_2$  at STP  
 (c) Water vapour at  $150^\circ\text{C}$  & 1 atm  
 $\Delta S > 0$

$$\Delta S = nR \ln \frac{V_2}{V_1} \text{ or } nR \ln \frac{P_1}{P_2}$$

Q.46  $19.09 \text{ JK}^{-1}$

Q.47 (i)  $\Delta S_{\text{gas}} = -\Delta S_{\text{surr}}$  and  $\Delta S_{\text{total}} = 0$ , (ii)  $\Delta S_{\text{total}} = 2.808 \text{ J K}^{-1}$  (iii)  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 9.134 \text{ J K}^{-1}$

Q.48 (i)  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 0$   
 (ii)  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 0.935 \text{ J/mol-K}$   
 (ii)  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 3.735 \text{ J/K}$

Q.49 (i) Rev. Process  $\Delta S_{\text{syst}} = \frac{3}{2} R \ln 10$ ;  $\Delta S_{\text{surr}} = -\frac{3}{2} R \ln 10$   
 (ii) Irr Process  $\Delta S_{\text{sys}} = \frac{3}{2} R \ln 10$ ;  $\Delta S_{\text{surr}} = -\frac{3}{2} R (0.9)$ ;  $\Delta S_{\text{total}} = \frac{3}{2} R (1.403)$

Q.50 (a)  $\Delta S_{\text{surr}} = -89.4 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $\Delta S_{\text{total}} = -2.4 \text{ JK}^{-1}\text{mol}^{-1}$  (– ve so nonspontaneous)  
 (b)  $\Delta S_{\text{surr}} = -87 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $\Delta S_{\text{total}} = 0$  (at equilibrium)  
 (c)  $\Delta S_{\text{surr}} = -84.49 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $\Delta S_{\text{total}} = +2.5 \text{ JK}^{-1}\text{mol}^{-1}$  (spontaneous)  
 (d)  $79.5^\circ\text{C}$

Q.51  $\Delta S^\circ_{\text{rxn}} = -327 \text{ JK}^{-1}$ ;  $\Delta S^\circ_{\text{surr}} = +2000 \text{ JK}^{-1}$ ;  $\Delta S^\circ_{\text{Total}} = 1673 \text{ JK}^{-1}$

Q.52  $\Delta S_{\text{sys}} = 244 \text{ JK}^{-1}$       Q.53  $\Delta H = q = +19.96 \text{ KJ}$ ;  $\Delta S = 57.23 \text{ JK}^{-1}$

Q.54  $-2800 \text{ kJ/mol}$       Q.55  $+2864.5 \text{ KJ}$       Q.56  $-1721.8 \text{ J}$

Q.57 (a)  $2.739 \text{ kJ}$ , (b)  $80 \text{ J}$  (c)  $90 \text{ J}$  (d)  $\Delta G_{\text{net}} = +8.82 \text{ J}$  (e)  $-4.2 \text{ kJ}$

Q.58  $3730 \text{ ln } 5 \text{ Cal}$       Q.59  $7.5 \text{ kJ}$       Q.60  $\Delta S = -36.5 \text{ J}$

Q.61

|   | $\Delta S$ | $\Delta H$ | $\Delta G$ | $\Delta S_{\text{total}}$ |
|---|------------|------------|------------|---------------------------|
| 1 | +          | +          | 0          | 0                         |
| 2 | +          | +          | –          | +                         |
| 3 | +          | +          | +          | –                         |
| 4 | +          | +          | +          | –                         |
| 5 | +          | +          | –          | +                         |
| 6 | +          | +          | 0          | 0                         |
| 7 | +          | +          | –          | +                         |
| 8 | +          | +          | +          | –                         |
| 9 | +          | +          | +          | –                         |

Q.62  $\Delta H^\circ = 9.04 \text{ kJ/mol}$ ;  $\Delta S^\circ = -8.64 \text{ J/mol}^{-1}\text{K}^{-1}$

Q.63  $1.21 \times 10^{-6}$       Q.69 (a) 26.4, (b) 7.2      Q.64  $\Delta G^\circ = -71.77 \text{ kJ/mol}$ ,  $\Delta G = 0$

Q.65 (a) Reaction is at equilibrium and  $Q_p = K_p = 10^6$   
 (b) Reaction is will move in forward direction.  
 (c) Reaction is will move in backward direction.  
 (d) Think by yourself.

Q.66  $K_p = 10^{200}$

Q.67 (a) Minima in the plot is equilibrium position.  
 (b) The quantity x is  $\Delta G^\circ$   
 (c) Minima on the right side of reaction indicate at equilibrium reaction is product favoured

### EXERCISE-2

(I)

1. T      2. T      3. F      4. T      5. T  
 6. T      7. F      8. T      9. F      10. T

(II)

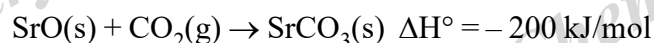
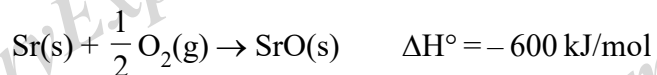
1. negative      2. isolated      3. two      4. reversible  
 5. decreasing      6. isentropic      7. Initial, final      8. decrease  
 9. zero      10. positive

(III)

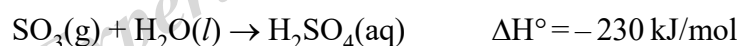
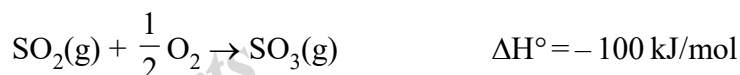
Q.1 C      Q.2 D      Q.3 B      Q.4 B      Q.5 D      Q.6 C      Q.7 B  
 Q.8 B      Q.9 C      Q.10 A      Q.11 B      Q.12 B      Q.13 D      Q.14 C  
 Q.15 B      Q.16 B      Q.17 C      Q.18 A      Q.19 C      Q.20 A      Q.21 B  
 Q.22 C      Q.23 C      Q.24 C      Q.25 C      Q.26 A      Q.27 D      Q.28 D  
 Q.29 D      Q.30 B      Q.31 A      Q.32 D      Q.33 A      Q.34 C      Q.35 D  
 Q.36 C      Q.37 C      Q.38 C      Q.39 A      Q.40 C      Q.41 A      Q.42 ABC  
 Q.43 ABD      Q.44 ACD      Q.45 BD      Q.46 ABCD      Q.47 CD      Q.48 ABD      Q.49 CD  
 Q.50 ACD      Q.51 AC      Q.52 C      Q.53 D      Q.54 A      Q.55 C      Q.56 B  
 Q.57 B      Q.58 (A) P,R,S (B) Q, S (C) Q, S (D) S  
 Q.59 (A)  $\rightarrow$  S (B)  $\rightarrow$  P, R (C)  $\rightarrow$  P, S (D)  $\rightarrow$  P, R      Q.60 (A) P,S (B) P,R,S (C) Q, (D) R,S

**EXERCISE-1 (Subjective Questions)****ENTHALPY OF FORMATION AND COMBUSTION**

Q.1 Calculate standard enthalpy of formation ( $\Delta_f H^\circ$ ) in KJ/mol of  $\text{SrCO}_3(\text{s})$  by given data :



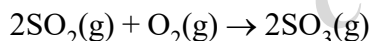
Q.2 Calculate enthalpy of formation of  $\text{H}_2\text{SO}_4(\text{aq})$  from following data :



$$\Delta_f H^\circ_{\text{SO}_2(\text{g})} = -300 \text{ kJ/mol}$$

$$\Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) = -170 \text{ kJ/mol}$$

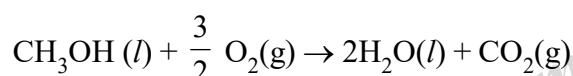
Q.3 Consider the reaction :



Carried out at  $27^\circ\text{C}$  and 1 atm. Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  &  $\Delta G^\circ$  for reaction using the following data :

| Substance               | $\Delta_f H^\circ$ (kJ/mol) | $S^\circ_m$ (J K <sup>-1</sup> mol <sup>-1</sup> ) |
|-------------------------|-----------------------------|----------------------------------------------------|
| $\text{SO}_2(\text{g})$ | -300                        | 250                                                |
| $\text{SO}_3(\text{g})$ | -400                        | 260                                                |
| $\text{O}_2(\text{g})$  | 0                           | 200                                                |

Q.4 For the reaction at  $27^\circ\text{C}$  :



| Substance                      | $\Delta_f H^\circ$ (kJ/mol) | $S^\circ_m$ (J/K-mol) | $\Delta_f G^\circ$ (kJ/mol) |
|--------------------------------|-----------------------------|-----------------------|-----------------------------|
| $\text{CH}_3\text{OH}$         | -238.5                      | 126                   | -166                        |
| $\text{H}_2\text{O}(\text{l})$ | -285.5                      | 70                    | -237                        |
| $\text{CO}_2(\text{g})$        | -393.5                      | 213                   | -394                        |

Calculate absolute entropy  $S^\circ$ , per mol of  $\text{O}_2(\text{g})$ .

Q.5 Use the thermodynamics parameter to estimate standard boiling point of methanol.

|                                                    | $\text{CH}_3\text{OH}(\text{l})$ | $\text{CH}_3\text{OH}(\text{g})$ |
|----------------------------------------------------|----------------------------------|----------------------------------|
| $\Delta_f G^\circ$ (kJ/mol)                        | -166                             | -162.5                           |
| $\Delta_f H^\circ$ (kJ/mol)                        | -237                             | -201                             |
| $S^\circ_m$ (JK <sup>-1</sup> -mol <sup>-1</sup> ) | +124                             | +244                             |

Q.6 (a) Write the chemical equation that defines the normal boiling of  $\text{CCl}_4(\text{l})$

(b) What is the value of  $\Delta G$  for the equilibrium in part(a)

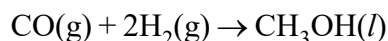
(c) Estimate normal boiling point of  $\text{CCl}_4$ .

[Given :  $\Delta_f H^\circ(\text{CCl}_4(\text{g})) = -100 \text{ kJ/mol}$ ,  $S^\circ_m(\text{CCl}_4(\text{g})) = 310 \text{ J/mol}$

$\Delta_f H^\circ(\text{CCl}_4(\text{l})) = -140 \text{ kJ/mol}$ ,  $S^\circ_m(\text{CCl}_4(\text{l})) = 210 \text{ J/mol}$  ]

Q.7 Given values of  $\Delta_f G^\circ$  at  $27^\circ\text{C}$  for liquid ethanol ( $-175 \text{ kJ/mol}$ ) and gaseous ethanol ( $-170 \text{ kJ/mol}$ ). Calculate vapour pressure of ethanol at  $27^\circ\text{C}$ . [ $\ln(0.13) = -2$ ] [ $R = 8.3 \text{ J/mol-K}$ ]

Q.8 One method of synthesizing methanol( $\text{CH}_3\text{OH}$ ) involves reacting gaseous carbon monoxide and hydrogen.

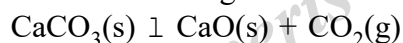


Calculate  $\Delta G$  at  $27^\circ\text{C}$  for this reaction, in which carbon monoxide gas at 5 atm and hydrogen gas at 2 atm are converted to liquid methanol.

[Given :  $\Delta_f G^\circ(\text{CH}_3\text{OH}) = -166 \text{ kJ}$ ,  $\Delta_f G^\circ(\text{CO(g)}) = -136 \text{ kJ}$ ]

[ $\ln 10 = 2.3$ ,  $\ln 2 = 0.7$ ,  $R = \frac{25}{3} \text{ J/mol-K}$ ]

Q.9 What is  $\Delta G^\circ$  for following reaction at  $1127^\circ\text{C}$  ?



|                           | $\Delta_f H^\circ \text{ (kJ/mol)}$ | $\Delta_f S^\circ \text{ (J/mol)}$ |
|---------------------------|-------------------------------------|------------------------------------|
| $\text{CaCO}_3\text{(s)}$ | -1222.94                            | 93                                 |
| $\text{CaO(s)}$           | -635                                | 38                                 |
| $\text{CO}_2\text{(g)}$   | -393.5                              | 213                                |

(a) Is this reaction spontaneous at  $1127^\circ\text{C}$  ?

(b) What is partial pressure of  $\text{CO}_2\text{(g)}$  at  $1127^\circ\text{C}$  ?

(c) What is the value of equilibrium constant ?

(d) At what minimum temperature decomposition of  $\text{CaCO}_3$  will take place?

(e) Is it entropy driven process or enthalpy driven process?

(f) In which direction reaction system will shift on increasing temperature?

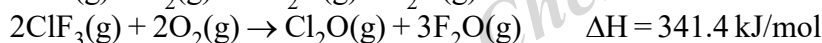
Q.10 When 2 moles of  $\text{C}_2\text{H}_6\text{(g)}$  are completely burnt 3120 kJ of heat is liberated. Calculate the enthalpy of formation, of  $\text{C}_2\text{H}_6\text{(g)}$ . Given  $\Delta_f H$  for  $\text{CO}_2\text{(g)}$  &  $\text{H}_2\text{O(l)}$  are -395 & -286 kJ respectively.

Q.11 Calculate standard enthalpies of formation of carbon-di-sulphide (l). Given the standard enthalpy of combustion of carbon (s), sulphur (s) & carbon-di-sulphide (l) are : -393.4, -293.3 and -1108 kJ mol<sup>-1</sup> respectively.

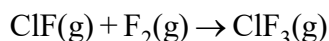
Q.12 From the following data at  $25^\circ\text{C}$ , Calculate the standard enthalpy of formation of  $\text{FeO(s)}$  and of  $\text{Fe}_2\text{O}_3\text{(s)}$ .

| Reaction                                                                                              | $\Delta_r H^\circ \text{ (kJ/mol)}$ |
|-------------------------------------------------------------------------------------------------------|-------------------------------------|
| (i) $\text{Fe}_2\text{O}_3\text{(s)} + 3\text{C(graphite)} \rightarrow 2\text{Fe(s)} + 3\text{CO(g)}$ | 492.5                               |
| (ii) $\text{FeO(s)} + \text{C(graphite)} \rightarrow \text{Fe(s)} + \text{CO(g)}$                     | 155.5                               |
| (iii) $\text{C(graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$                   | -393.5                              |
| (iv) $\text{CO(g)} + 1/2 \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$                      | -283                                |

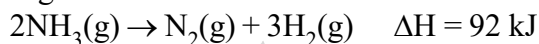
Q.13 Given the following data :



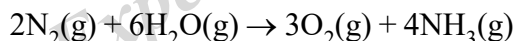
Calculate  $\Delta H$  for the reaction



Q.14 Given the following data :



Calculate  $\Delta H$  for the reaction :



Q.15 The enthalpy change for the reaction  $\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g})$  at  $25^\circ \text{C}$  is  $-55.8 \text{ kJ/mol}$ . Calculate the enthalpy of combustion of  $\text{C}_2\text{H}_6(\text{g})$ . The enthalpy of combustion of  $\text{H}_2$ , &  $\text{CH}_4$  are  $-285.8$  &  $-890.0 \text{ kJ/mol}$  respectively. Enthalpy of combustion of propane is  $-2220 \text{ kJ mol}^{-1}$ .

Q.16 At  $300 \text{ K}$ , the standard enthalpies of formation of  $\text{C}_6\text{H}_5\text{COOH}(\text{s})$ ,  $\text{CO}_2(\text{g})$  &  $\text{H}_2\text{O}(\text{l})$  are ;  $-408$ ,  $-393$  &  $-286 \text{ kJ mol}^{-1}$  respectively .

Calculate the heat of combustion of benzoic acid at:

(a) constant pressure

(b) constant volume.

Q.17 Calculate the mass of mercury which can be liberated from  $\text{HgO}$  at  $27^\circ \text{C}$  by the treatment of excess  $\text{HgO}$  with  $45.4 \text{ kJ}$  of heat at :

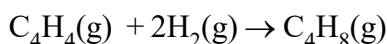
(a) constant pressure

(b) constant volume

**Given :**  $\Delta H_f^\circ (\text{HgO}, \text{s}) = -90.8 \text{ kJ mol}^{-1}$  &  $M(\text{Hg}) = 200.6 \text{ g mol}^{-1}$  .

Q.18 It is observed that on combustion of  $5.6 \text{ gm}$  of but - 1-ene(g),  $70 \text{ Kcal}$  of heat is liberated in a closed rigid vessel at  $300 \text{ K}$ . What could be a theoretical value of  $\Delta H_{\text{combustion}}^\circ$  of but-2-ene at same temperature.

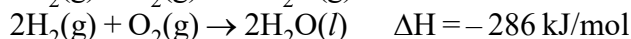
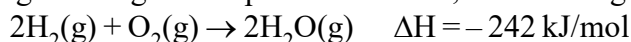
Q.19 Calculate  $\Delta H$  for the reaction



**Given :**  $\Delta_c H^\circ (\text{C}_4\text{H}_4(\text{g})) = 22340 \text{ kJ/mol}$        $\Delta_c H^\circ (\text{H}_2(\text{g})) = 22755 \text{ kJ/mol}$

$\Delta_c H^\circ (\text{C}_4\text{H}_8(\text{g})) = 2286 \text{ kJ/mol}$

Q.20 When hydrogen gas undergoes complete combustion, the following enthalpy values are obtained :



Calculate  $\Delta H$  for  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

Q.21 Three isomers with formula  $\text{C}_4\text{H}_8$  their enthalpy of combustion data is given as :

**Compound**       **$\Delta_c H(\text{kJ/mol})$**

cis-2-butene       $-2687.5$

trans-2-butene       $-2684.2$

1-butene       $-2696.2$

What is the enthalpy change for conversion of cis-2-butene to trans-2-butene?

### OTHER TYPES OF ENTHALPY OF REACTION

Q.22 If the enthalpy of formation of  $\text{HCl}(\text{g})$  and  $\text{Cl}^-(\text{aq})$  are  $-92.3 \text{ kJ/mol}$  and  $-167.3 \text{ kJ/mol}$ , find the enthalpy of solution of hydrogen chloride gas.



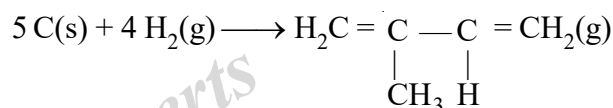
- Q.23 The lattice enthalpy of AgF is 958 kJ/mol and AgCl is 905 kJ/mol. The enthalpy of hydration of  $\text{Ag}^+(\text{g})$  is  $-446$  kJ/mol, that of  $\text{F}^-$  is  $-506$  kJ/mol and that of  $\text{Cl}^-(\text{g})$  is  $-364$  kJ/mol. Calculate the  $\Delta_{\text{sol}}H$  of AgCl(s) and AgF(s).
- Q.24 The enthalpy of solution of anhydrous  $\text{CuSO}_4$  is  $-15.9$  kCal and that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is  $2.8$  kCal. Calculate the enthalpy of hydration of  $\text{CuSO}_4$ .
- Q.25 The enthalpies of neutralization of NaOH &  $\text{NH}_4\text{OH}$  by HCl are  $-13680$  Cal and  $-12270$  Cal respectively. What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of  $\text{NH}_4\text{Cl}$  in solution? Assume that  $\text{NH}_4\text{OH}$  and NaCl are quantitatively obtained.
- Q.26 From the data of  $\Delta H$  of the following reactions  

$$\text{C}(\text{s}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) ; \Delta H = -110 \text{ kJ}$$
and 
$$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}) ; \Delta H = 130 \text{ kJ}$$
Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at  $1273 \text{ K}$ , keeping the reaction temperature constant and there is no heat exchange with surrounding.
- Q.27 The polymerisation of ethylene to linear polyethylene is represented by the reaction  

$$n\text{CH}_2 = \text{CH}_2 \rightarrow (-\text{CH}_2 - \text{CH}_2 -)_n$$
where  $n$  has a large integral value. Given that the average enthalpies of bond dissociation for  $\text{C}=\text{C}$  &  $\text{C}-\text{C}$  at  $298 \text{ K}$  are  $+590$  &  $+331 \text{ kJ mol}^{-1}$  respectively. Calculate the enthalpy of polymerisation per mole of ethylene at  $298 \text{ K}$ .
- Q.28 The enthalpies of neutralization of a weak acid HA & a weak acid HB by NaOH are  $-6900$  Cal/equivalent &  $-2900$  Cal/equivalent respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was  $-3900$  Calories. In what ratio is the base distributed between HA & HB?

### BOND ENTHALPY

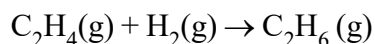
- Q.29 Using bond enthalpy data, calculate enthalpy of formation of isoprene. Neglect resonance in isoprene.



**Given :**  $\text{C}-\text{H} = 98.5 \text{ k Cal}$  ;  $\text{H}-\text{H} = 104 \text{ k Cal}$  ;  
 $\text{C}-\text{C} = 83 \text{ k Cal}$  ;  $\text{C}=\text{C} = 147 \text{ k Cal}$  &  
 $\text{C}(\text{s}) \rightarrow \text{C}(\text{g}) = 171 \text{ k Cal}$  .

- Q.30 The enthalpy of atomization of  $\text{PH}_3$  is  $954 \text{ kJ mol}^{-1}$  and that of  $\text{P}_2\text{H}_4$  is  $1.485 \text{ MJ mol}^{-1}$ . What is the bond enthalpy of the P-P bond?

Q.31 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.



**Data:**

| Bond          | C—C        | C = C      | C—H          | H—H          |
|---------------|------------|------------|--------------|--------------|
| Bond Enthalpy | 337 kJ/mol | 606 kJ/mol | 410.4 kJ/mol | 431.8 kJ/mol |

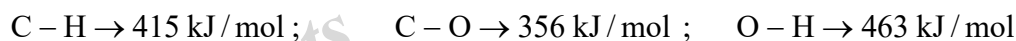
Q.32 Compute the enthalpy of formation of liquid methyl alcohol in  $\text{kJ mol}^{-1}$ , using the following data.

Enthalpy of vaporisation of liquid  $\text{CH}_3\text{OH} = 38 \text{ kJ/mol}$ .

Enthalpy of formation of gaseous atoms from the elements in their standard states are



Average Bond energies



Q.33 From the following data :

Enthalpy of formation of  $\text{CH}_3\text{CN} = 90 \text{ kJ/mol}$

Enthalpy of formation of  $\text{C}_2\text{H}_6 = -85 \text{ kJ/mol}$

Enthalpy of sublimation of graphite =  $720 \text{ kJ/mol}$

Enthalpy of dissociation of nitrogen =  $945 \text{ kJ/mol}$

Enthalpy of dissociation of  $\text{H}_2 = 435 \text{ kJ/mol}$

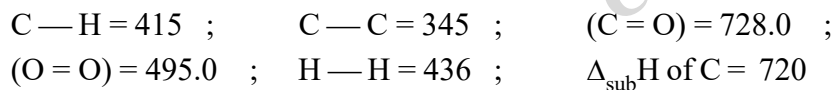
C—H bond enthalpy =  $415 \text{ kJ/mol}$

Calculate the bond enthalpy of (i) C—C ; (ii)  $\text{C} \equiv \text{N}$

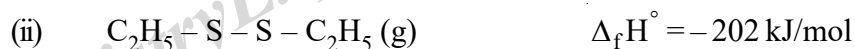
Q.34 The enthalpy of combustion of acetylene is  $-312 \text{ kcal}$  per mole. If enthalpy of formation of  $\text{CO}_2$  &  $\text{H}_2\text{O}$  are  $-94.5$  &  $-68 \text{ kcal}$  per mole respectively, calculate  $\text{C} \equiv \text{C}$  bond enthalpy.

Given that enthalpy of atomisation of C is  $150 \text{ kcal}$  per mole and H—H bond enthalpy and C—H bond enthalpy are  $103 \text{ kcal}$  per mole and  $93.50 \text{ kcal}$  per mole respectively.

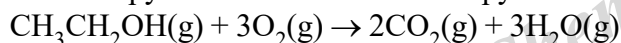
Q.35 Using the given data calculate enthalpy of formation of acetone (g). [All values in  $\text{kJ mol}^{-1}$ ]  
bond enthalpy of :



Q.36 Find the enthalpy of S—S bond from the following data.



Q.37 Use the mean bond enthalpy data to calculate the enthalpy of combustion of ethanol.



[Given : Bond energy (C—H) =  $412 \text{ kJ/mol}$  ; (C=O) =  $743 \text{ kJ/mol}$

(C—C) =  $348 \text{ kJ/mol}$  ; (C—O) =  $360 \text{ kJ/mol}$

(O=O) =  $496 \text{ kJ/mol}$  ; (O—H) =  $463 \text{ kJ/mol}$

**RESONANCE ENERGY**

- Q.38 Calculate resonance energy of  $\text{CO}_{2(g)}$  from the following data.
- |                                                                        |                                                          |
|------------------------------------------------------------------------|----------------------------------------------------------|
| $\Delta H_{\text{combustion}}$ of CO = $-280 \text{ kJ/mol}$           | $\Delta H_f$ CO = $-120 \text{ kJ/mol}$                  |
| $\Delta H_{\text{atomisation}}$ of C (graphite) = $720 \text{ kJ/mol}$ | $\Delta H_{\text{BE}}$ O = O = $500 \text{ kJ mol}^{-1}$ |
|                                                                        | $\Delta H_{\text{BE}}$ C = O = $710 \text{ kJ/mol}$      |
- Q.39 Calculate the enthalpy of combustion of methyl alcohol at 298 K from the following data
- |                                       |       |       |       |       |       |
|---------------------------------------|-------|-------|-------|-------|-------|
| Bond                                  | C – H | C – O | O – H | O = O | C = O |
| Bond Enthalpy( $\text{kJ mol}^{-1}$ ) | 415   | 352   | 465   | 494   | 710   |
- Resonance energy of  $\text{CO}_2 = -143 \text{ kJ mol}^{-1}$   
 Latent heat of vaporisation of methyl alcohol =  $35.5 \text{ kJ mol}^{-1}$ .  
 Latent heat of vaporisation of water =  $40.5 \text{ kJ mol}^{-1}$ .
- Q.40 What will be the value of resonance energy of  $\text{N}_2\text{O}$  if
- |                                                               |                                                                  |
|---------------------------------------------------------------|------------------------------------------------------------------|
| $\Delta H_{\text{BDE}}$ N = N = $400 \text{ kJ/mol}$ ;        | $\Delta H_f^\circ \text{ N}_2\text{O} = 100 \text{ kJ mol}^{-1}$ |
| $\Delta H_{\text{BDE}}$ N $\equiv$ N = $950 \text{ kJ/mol}$ ; | $\Delta H_{\text{BDE}}$ N = O = $600 \text{ kJ mol}^{-1}$        |
| $\Delta H_{\text{BDE}}$ O = O = $500 \text{ kJ/mol}$          |                                                                  |

**CALORIMETERY**

- Q.41 0.16 g of methane was subjected to combustion at  $27^\circ\text{C}$  in a bomb Calorimeter. The temperature of Calorimeter system (including water) was found to rise by  $0.5^\circ\text{C}$ . Calculate the heat of combustion of methane at
- constant volume
  - constant pressure.
- The thermal capacity of Calorimeter system is  $17.7 \text{ kJ K}^{-1}$ . ( $R = \frac{25}{3} \text{ J mol}^{-1} \text{ K}^{-1}$ )
- Q.42 When 0.2 mol of ethane is burnt completely in a bomb calorimeter, the temperature of calorimeter system increased by 2 K. What should be the increase in temperature of the same calorimeter system, when 0.4 mol of  $\text{CH}_4$  is burnt?
- [Given :  $\Delta_c U_{\text{C}_2\text{H}_6(g)} = -400 \text{ Kcal/mol}$  and  $\Delta_c U_{\text{CH}_4(g)} = -200 \text{ Kcal/mol}$ ]
- Q.43 Two solutions initially at  $25^\circ\text{C}$  were mixed in an adiabatic constant pressure Calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to  $26.2^\circ\text{C}$ . How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution  $1.0 \text{ g/cm}^3$ , and specific heat of solution  $4.0 \text{ J/g}\cdot\text{K}$ . Neglect heat capacity of the Calorimeter.
- Q.44 Benzoic acid is a common standard used in Bomb calorimeters, which maintain a constant volume. If 1.22 gm of benzoic acid gives off 31.7 J of energy when burned in the presence of just sufficient oxygen at an initial temperature of  $24.6^\circ\text{C}$ , calculate molar heat capacity at constant volume of final product mixture if all the heat produce is used for increasing temperature of the final product mixture and the final temperature is  $49.6^\circ\text{C}$ . Also calculate, w and  $\Delta U$  for the given amount, assuming ideal gas behaviour.

KIRCHOFF'S EQUATION

Q.45 For a reaction :  $2A + 3B \rightarrow C + D$   $\Delta H_{300}^{\circ} = 30 \text{ kJ/mol}$ ;  $\Delta S_{300}^{\circ} = 20 \text{ J/K mol}$

If molar heat capacities at constant pressure are given as :

$$C_{P,m} A = 10 \text{ J/mol K};$$

$$C_{P,m} B = 15 \text{ J/mol K}$$

$$C_{P,m} C = 25 \text{ J/mol K};$$

$$C_{P,m} D = 20 \text{ J/mol K}$$

Then calculate  $|\Delta S_{\text{universe}}^{\circ}|$  (in J/k) if the above reaction is carried out at 400K.  $\left(\ln\left(\frac{4}{3}\right) = 0.28\right)$

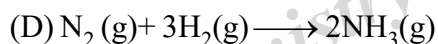
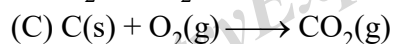
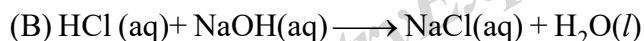
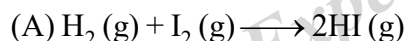
**[Round off to nearest integer ]**

Q.46 The standard enthalpy for the reaction  $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$  is  $-285.76 \text{ kJ}$  at  $298 \text{ K}$ . Calculate the value of  $\Delta H$  at  $373 \text{ K}$ . The molar heat capacities at constant pressure ( $C_p$ ) in the given temperature range of  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are respectively  $38.83$ ,  $29.16$  and  $75.312 \text{ JK}^{-1}\text{mol}^{-1}$ .

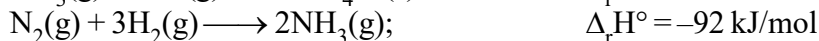
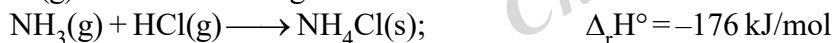
Q.47 At  $298 \text{ K}$ ,  $\Delta H_{\text{combustion}}^{\circ}(\text{sucrose}) = -5737 \text{ KJ/mol}$  &  $\Delta G_{\text{combustion}}^{\circ}(\text{sucrose}) = -6333 \text{ KJ/mol}$ . Estimate additional non-PV work that is obtained by raising temperature to  $310 \text{ K}$ . Assume  $\Delta_r C_p = 0$  for this temperature change

**EXERCISE-2 (Objective Questions)****Single correct**

Q.1 For which of the following change  $\Delta H$  not equal to  $\Delta E$ ?



Q.2 Find  $\Delta_f H^\circ$  for  $\text{HCl}(\text{g})$  from the following data:



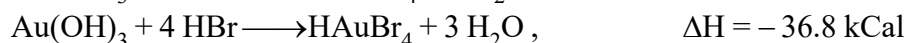
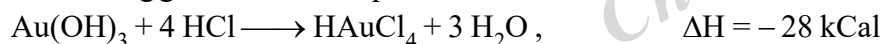
(A) 536.5 kJ/mol (B) -361 kJ/mol (C) -92.5 kJ/mol (D) None

Q.3 Calculate  $\Delta H^\circ_{\text{combustion}}$  of acetone if  $\Delta H^\circ_f$  of acetone = -250 kJ

$\Delta H^\circ_{\text{combustion}}$  of  $\text{C}_{\text{graphite}} = -390 \text{ kJ/mol}$  &  $\Delta H^\circ_{\text{combustion}}$  of  $\text{H}_{2(\text{g})} = -280 \text{ kJ/mol}$ :

(A) -1230 kJ/mol (B) -1760 kJ/mol (C) -1370 kJ/mol (D) -1410 kJ/mol

Q.4 Reactions involving gold have been of particular interest to a chemist. Consider the following reactions,



In an experiment there was an absorption of 0.44 kCal when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of  $\text{HCl}$ . What is the percentage conversion of  $\text{HAuBr}_4$  into  $\text{HAuCl}_4$ ?

(A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 %

Q.5 The enthalpy of tetramerization of X in gas phase ( $4\text{X}(\text{g}) \longrightarrow \text{X}_4(\text{g})$ ) is -100 kJ/mol at 300 K. The enthalpy of vaporisation for liquid X and  $\text{X}_4$  are respectively 30 kJ/mol and 72 kJ/mol respectively.  $\Delta S$  for tetramerization of X in liquid phase is -125 J / K mol at 300 K.

What is the  $\Delta G$  at 300 K for tetramerization of X in liquid phase?

(A) -52 kJ/mol (B) -89.5 kJ/mol  
(C) -14.5 kJ/mol (D) None of these

Q.6 The reaction  $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$  has  $\Delta H = -25 \text{ kCal}$ .

| Bond                      | Bond Energy kCal |
|---------------------------|------------------|
| $\epsilon_{\text{C-Cl}}$  | 84               |
| $\epsilon_{\text{H-Cl}}$  | 109              |
| $\epsilon_{\text{C-H}}$   | x                |
| $\epsilon_{\text{Cl-Cl}}$ | y                |
| x : y = 9 : 5             |                  |

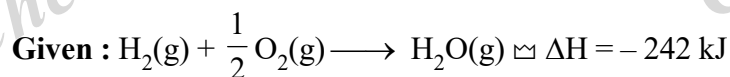
From the given data, what is the bond enthalpy of  $\text{Cl-Cl}$  bond

(A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 60 kCal

- Q.7 Calculate C – H Bond energy from the following data :  
 $\Delta_f H(C, g) = 716.68 \text{ kJ/mol}$      $\Delta_f H(H, g) = 217.97 \text{ kJ/mol}$      $\Delta_f H(CH_4, g) = -74.81 \text{ kJ/mol}$   
 (A) 1663.37 kJ    (B) 415.84 kJ    (C) 179.17 kJ    (D) 74.81 kJ
- Q.8 Which of the following reactions defines  $\Delta H_f^\circ$  ?  
 (A)  $C_{(\text{diamond})} + O_2(g) \longrightarrow CO_2(g)$     (B)  $1/2 H_2(g) + 1/2 F_2(g) \longrightarrow HF(g)$   
 (C)  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3$     (D)  $CO(g) + 1/2 O_2(g) \longrightarrow CO_2(g)$
- Q.9 For the allotropic change represented by the equation  $C(\text{graphite}) \rightarrow C(\text{diamond})$ ,  $\Delta H = 1.9 \text{ kJ}$ . If 6 g of diamond and 6 g of graphite are separately burnt to yield  $CO_2$ , the enthalpy liberated in first case is  
 (A) less than in the second case by 1.9 kJ    (B) more than in the second case by 11.4 kJ  
 (C) more than in the second case by 0.95 kJ    (D) less than in the second case by 11.4 kJ
- Q.10 Find  $\Delta_r U^\circ$  for the reaction  $4HCl(g) + O_2(g) \longrightarrow 2Cl_2(g) + 2H_2O(g)$  at 300 K. Assume all gases are ideal.  
**Given:**  $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$      $\Delta_r H_{300}^\circ = -184.5 \text{ kJ/mol}$   
 $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$      $\Delta_r H_{300}^\circ = -483 \text{ kJ/mol}$  (Use  $R = 8.3 \text{ J/mol}$ )  
 (A) 111.5 kJ/mol    (B) -109.01 kJ/mol    (C) -111.5 kJ/mol    (D) None
- Q.11 Which of the following represent standard formation reaction of given compound?  
 (A)  $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$     (B)  $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$   
 (C)  $\frac{1}{2} H_2(g) + (aq) \rightarrow H^+(aq) + 1e^-$     (D)  $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- Q.12 The combustion 1.22g benzoic acid ( $M = 122$ ) in a bomb calorimeter at 300K caused a temperature rise of 3K, while combustion of 0.88g ethyl ethanoate ( $M = 88$ ) caused a temperature rise of 2K. Calculate the enthalpy change of combustion of  $CH_3COOC_2H_5(l)$  at 300K.  
**Given :** Internal energy change of combustion for benzoic acid =  $-3000 \text{ kJ mol}^{-1}$  at 300K  
 (A) -2000 kJ    (B) -2002.49 kJ    (C) -2006.5 kJ    (D) -3002.5 kJ
- Q.13 In order to solve a complex physical chemistry problem, brain requires some "neural energies" which are electrical in nature. Each problem on an average requires 21 Joules of neural energy. Calculate minimum amount of glucose required to solve 10 such problems if all electrical energy is obtained from oxidation of glucose.  
**[Given :**  $\Delta H_{\text{combustion}}^\circ$  of glucose =  $-2800 \text{ kJ/mole}$ ,  $\Delta S_{\text{combustion}}^\circ$  of glucose =  $-\frac{1000}{3} \text{ J/molK}$ ,  
 Temperature = 300K ]  
 (A) 14 mg    (B) 14 mg    (C) 20 gm    (D) 120 mg
- Q.14 The lattice enthalpy of solid NaCl is  $772 \text{ kJ mol}^{-1}$  and enthalpy of solution is  $2 \text{ kJ mol}^{-1}$ . If the hydration enthalpy of  $Na^+$  &  $Cl^-$  ions are in the ratio of 3:2.5, what is the enthalpy of hydration of chloride ion?  
 (A)  $-140 \text{ kJ mol}^{-1}$     (B)  $-350 \text{ kJ mol}^{-1}$     (C)  $-351.81 \text{ kJ mol}^{-1}$     (D) None

- Q.15 The molar heat capacities at constant pressure (assume constant with respect to temperature) of A, B and C are in ratio of **1.5 : 3.0 : 2.0**. If enthalpy change for the exothermic reaction  $A + 2B \longrightarrow 3C$  at 300 K is  $-10 \text{ kJ/mol}$  &  $C_{p,m}$  (B) is  $300 \text{ J/mol}$  then enthalpy change at 310 K is :  
 (A)  $-8.5 \text{ kJ/mol}$  (B)  $8.5 \text{ kJ/mol}$  (C)  $-11.5 \text{ kJ/mol}$  (D) none of these

- Q.16 What is the ratio of the enthalpy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam?



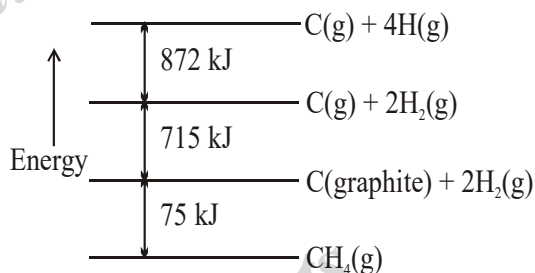
B.E. (H-H) =  $436 \text{ kJ}$

- (A)  $0.80 : 1$  (B)  $1 : 0.80$  (C)  $1.80 : 1$  (D)  $2.80 : 1$
- Q.17  $\Delta H_f^\circ$  of water is  $-285.8 \text{ kJ mol}^{-1}$ . If enthalpy of neutralisation of monoacid strong base is  $-57.3 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ$  of  $\text{OH}^-$  ion will be  
 (A)  $-228.5 \text{ kJ mol}^{-1}$  (B)  $228.5 \text{ kJ mol}^{-1}$  (C)  $114.25 \text{ kJ mol}^{-1}$  (D)  $-114.25 \text{ kJ mol}^{-1}$

- Q.18 Select the correct option.

- (A)  $\Delta H_f[\text{H}(\text{g})]$  is equal to  $\Delta H_{\text{atomisation}}$  of  $\text{H}_2(\text{g})$   
 (B)  $\Delta H_{\text{BE}}(\text{H-H})$  is equal to  $\Delta H_f$  of  $\text{H}(\text{g})$   
 (C)  $\Delta H_{\text{BE}}(\text{H-H})$  is equal to  $\Delta H_{\text{atomisation}}$  of  $\text{H}_2(\text{g})$   
 (D)  $\Delta H_{\text{combustion}}[\text{H}_2(\text{g})]$  is equal to  $\Delta H_f[\text{H}_2(\text{g})]$

- Q.19 From following Born Haber cycle, identify **incorrect** statement :



- (A)  $\Delta_f H(\text{CH}_4) = -75 \text{ kJ}$  (B) Bond energy of (C-H) =  $145 \text{ kJ/mol}$   
 (C)  $\Delta_{\text{sublimation}} H$  of C =  $715 \text{ kJ/mol}$  (D)  $\Delta_{\text{formation}} H$  of  $\text{H}(\text{g}) = 218 \text{ kJ/mol}$

- Q.20 Study the following thermochemical equations:



The correct order of enthalpies of formation of A, B and C is

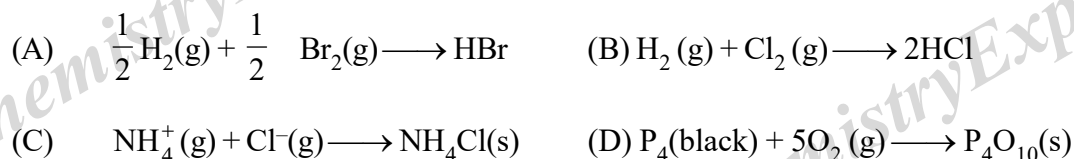
- (A)  $A < B < C$  (B)  $A < C < B$  (C)  $C < A < B$  (D)  $B < C < A$



- Q.21  $\Delta H_f^\circ$  of atomic B is 134.5 Kcal/mol and  $\Delta H_f^\circ$  of atomic F is 118 Kcal/mol.  $\Delta H_f^\circ$  of  $\text{BF}_3(\text{g})$  is  $-271.5$  Kcal/mol. Average B–F energy would be  
 (A) 97.7 Kcal/mol (B) 116.6 Kcal/mol (C) 135.4 Kcal/mol (D) 253.3 Kcal/mol
- Q.22 Calculate enthalpy of combustion of propane [ $\text{C}_3\text{H}_8(\text{g})$ ] in kJ/mol at 298 K.  
**Given :** B.E.(O = O) = 498 kJ/mol ; B.E. (C = O) = 804 kJ/mol  
 B.E. (C–H) = 410 kJ/mol ; B.E.(O–H) = 464 kJ/mol  
 B.E. (C–C) = 345 kJ/mol ; Resonance energy of  $\text{CO}_2(\text{g}) = -143$  kJ/mol  
 $\Delta H_{\text{vaporization}}(\text{H}_2\text{O}, l) = 41$  kJ/mol  
 (A)  $-1996$  (B)  $-2669$  (C)  $-2324$  (D) None of these
- Q.23 For a reaction :  $2\text{A}_{(\text{g})} + \text{B}_{(\text{g})} \longrightarrow \text{C}_{(\text{g})}$ ,  $\Delta U^\circ = 30$  Kcal/mol,  $\Delta S^\circ = 100$  cal/K mol at 300K. What will be the value of  $\Delta G^\circ_{\text{rxn}}$  at 400K? [ $R = 2$  cal/K mol] [ $\Delta C_{p_{\text{rxn}}} = 0$ ]  
 (A) 0 (B)  $-1.2$  Kcal (C)  $-11.2$  Kcal (D)  $-10$  Kcal
- Q.24 0.2 M, 100 ml NaOH is mixed with 0.4 M, 100 ml HCl solution. Determine energy released during the reaction.  
**Given :**  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(l)$  ;  $\Delta H = -57.5$  kJ mol $^{-1}$   
 (A) 1150 J (B) 1150 kJ (C) 2300 J (D) 2300 kJ
- Q.25 Enthalpy of neutralization of  $\text{H}_3\text{PO}_3$  acid is  $-106.68$  kJ/mol using NaOH. If enthalpy of neutralization of HCl by NaOH is  $-55.84$  kJ/mol. Calculate  $\Delta H_{\text{ionization}}$  of  $\text{H}_3\text{PO}_3$  into its ions  
 (A) 50.84 kJ/mol (B) 5 kJ/mol (C) 2.5 kJ/mol (D) None
- Q.26 When 100 ml 0.2 M KOH is mixed with 100 ml 0.2 M HCl, temperature of solution increases by  $t_1^\circ\text{C}$  while when 300 ml 0.1 M KOH is mixed with 300 ml 0.1 M HCl then increase in temperature is  $t_2^\circ\text{C}$  then which one is correct. (Assuming density as well as specific heat of final solutions are same)  
 (A)  $t_1 = t_2$  (B)  $t_1 > t_2$  (C)  $t_1 < t_2$  (D) Can't be predicted
- Q.27 The value of change in enthalpy for 1 mole of  $\text{H}_2\text{O}$  in  
 $\text{H}_2\text{O}(l, 1 \text{ atm}, 373\text{K}) \rightarrow \text{H}_2\text{O}(g, 1 \text{ atm}, 393 \text{ K})$   
**Given :**  $C_p(\text{H}_2\text{O}, l) = 75.3 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $C_p(\text{H}_2\text{O}, g) = 35 \text{ JK}^{-1}\text{mol}^{-1}$ ,  
 $\Delta_{\text{vap}}H$  at 373K = 40 kJ/mol  
 (A) 740 kJ (B) 39.3 kJ (C) 40.7 kJ (D) 740 J

**More than one may correct**

- Q.28 Which of the following do(es) not represent  $\Delta H$  formation of the product.



- Q.29 Which of the following is **correct** for boiling of  $\text{CCl}_4(l)$  at its standard boiling point?  
 (A)  $\Delta G = 0$  (B)  $\Delta G^\circ = 0$  (C)  $\Delta S^\circ > 0$  (D)  $\Delta H^\circ_{\text{vap}} > 0$



Q.30 From the following data at 25°C

| Reaction                                                                                                  | $\Delta_r H^\circ$ kJ/mol |
|-----------------------------------------------------------------------------------------------------------|---------------------------|
| $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{OH}(\text{g})$ | 42                        |
| $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g})$    | -242                      |
| $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$                                                | 436                       |
| $\text{O}_2(\text{g}) \longrightarrow 2\text{O}(\text{g})$                                                | 495                       |

Which of the following statement(s) is/are **correct** :

- (A)  $\Delta_r H^\circ$  for the reaction  $\text{H}_2\text{O}(\text{g}) \longrightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$  is 925.5 kJ/mol  
 (B)  $\Delta_r H^\circ$  for the reaction  $\text{OH}(\text{g}) \longrightarrow \text{H}(\text{g}) + \text{O}(\text{g})$  is 502 kJ/mol  
 (C) Enthalpy of formation of  $\text{H}(\text{g})$  is -218 kJ/mol  
 (D) Enthalpy of formation of  $\text{OH}(\text{g})$  is 42 kJ/mol

Q.31 100 ml 0.25 M  $\text{H}_2\text{SO}_4$  (strong acid) is neutralised with 200 ml 0.2M  $\text{NH}_4\text{OH}$  in a constant pressure Calorimeter which results in temperature rise of 1.4 °C. If heat capacity of Calorimeter content is 1.5 kJ/°C. Which statement is/are correct

**Given :**  $\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + 57 \text{ kJ}$   
 $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \longrightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O} + 48.1 \text{ kJ}$

- (A) Enthalpy of neutralisation of  $\text{HCl}$  v/s  $\text{NH}_4\text{OH}$  is - 52.5 kJ/mol  
 (B) Enthalpy of dissociation (ionization) of  $\text{NH}_4\text{OH}$  is 4.5 kJ/mol  
 (C) Enthalpy of dissociation of  $\text{CH}_3\text{COOH}$  is 4.6 kJ/mol  
 (D)  $\Delta H$  for  $2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{H}^+(\text{aq.}) + 2\text{OH}^-(\text{aq.})$  is 114 kJ

### Assertion Reason

Q.32 **Statement-1** : The enthalpy of neutralization of the reaction between  $\text{HCl}$  and  $\text{NaOH}$  is - 13.7 kCal / mol. If the enthalpy of neutralization of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) by a strong base is - 25.4 kCal / mol, then the enthalpy change (  $|\Delta_r H|$  ) of the process  $\text{H}_2\text{C}_2\text{O}_4 \longrightarrow 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$  is 11.7 kCal / mol.

**Statement-2** :  $\text{H}_2\text{C}_2\text{O}_4$  is a weak acid.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

Q.33 **Statement-1:** Standard enthalpy of isomerisation of an enantiomer into the other is zero.

**Statement-2:** The two enantiomers of any chiral compound have the same enthalpy of formation.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

## EXERCISE-1

- Q.1  $-1200 \text{ kJ/mol}$       Q.2  $-800 \text{ kJ/mol}$
- Q.3  $\Delta H_{\text{rxn}}^{\circ} = -200 \text{ kJ/mol}$ ,  $\Delta S_{\text{rxn}}^{\circ} = -180 \text{ J/K}$ ,  $\Delta G^{\circ} = -146 \text{ kJ/mol}$
- Q.4  $204.67 \text{ J/K-mol}$       Q.5  $T = 300 \text{ K}$
- Q.6 (a)  $\text{CCl}_4(l) \rightleftharpoons \text{CCl}_4(g)$  (Equilibrium at 1 atm pressure)  
(b)  $\Delta G = 0$   
(c)  $400 \text{ K}$
- Q.7 Vapour pressure =  $0.13 \text{ bar}$ .      Q.8  $-37.5 \text{ kJ/mol}$
- Q.9 (a) YES, As  $\Delta G_{\text{rxn}}^{\circ} = -ve$  ie reaction is spontaneous at  $1127^{\circ}\text{C}$ ,  
(b)  $10 \text{ bar}$       (c)  $10 \text{ bar}$       (d)  $1230.6 \text{ K}$   
(e) It is entropy driven process  
(f) In forward direction
- Q.10  $-88 \text{ kJ/mol}$
- Q.11  $128 \text{ kJ}$       Q.12  $-266 \text{ kJ/mol}$  and  $-824 \text{ kJ/mol}$       Q.13  $-108.7 \text{ kJ/mol}$
- Q.14  $-40 \text{ kJ/mol}$       Q.15  $-1560 \text{ kJ mol}^{-1}$
- Q.16 (a)  $-3201 \text{ kJ/mol}$ ; (b)  $-3199.75 \text{ kJ/mol}$
- Q.17 (a)  $100.3 \text{ g}$ ; (b)  $101.69 \text{ g}$       Q.18  $-700 \text{ Kcal/mol}$
- Q.19  $65564 \text{ kJ/mol}$       Q.20  $22 \text{ kJ/mol}$
- Q.21 Cis-2-butene  $\longrightarrow$  Trans-2-butene       $\Delta H_r = ?$   
 $\Delta_r H = -3.3 \text{ kJ/mol}$
- Q.22  $-75 \text{ kJ/mol}$       Q.23  $\Delta_{\text{sol}} H$  of  $\text{AgF}(s) = 6 \text{ kJ/mol}$ ;       $\Delta H_{\text{soln}} \text{AgCl} = 95 \text{ kJ/mol}$
- Q.24  $-18.7 \text{ kCal/mol}$       Q.25  $-1410 \text{ Cal}$
- Q.26 mole %  $\text{O}_2(g) = 37.14$ ,  $\text{H}_2\text{O}(g) = 62.86$       Q.27  $-72 \text{ kJ mol}^{-1}$
- Q.28  $1:3$       Q.29  $+23 \text{ kCal}$       Q.30  $213 \text{ kJ/mol}$
- Q.31  $-120 \text{ kJ/mol}$       Q.32  $-266 \text{ kJ mol}^{-1}$       Q.33 (i)  $340 \text{ kJ/mol}^{-1}$ ; (ii)  $890 \text{ kJ/mol}^{-1}$
- Q.34  $E_{\text{C}^{\circ}\text{C}} = 161 \text{ kCal/mol}$       Q.35  $-192.5 \text{ kJ mol}^{-1}$       Q.36  $280 \text{ kJ/mol}$
- Q.37  $-1031 \text{ kJ/mol}$       Q.38  $200 \text{ kJ}$       Q.39  $-665.5 \text{ kJ mol}^{-1}$
- Q.40  $100 \text{ kJ/mol}$       Q.41 (a)  $-885 \text{ kJ/mol}$  (b)  $-890 \text{ kJ/mol}$       Q.42  $2 \text{ K}$
- Q.43  $-30 \text{ kJ/mol}$       Q.44  $C = 12.68 \text{ J/mole-K}$ ,  $w = 0$ ,  $\Delta U = -31.7 \text{ J}$
- Q.45  $56$       Q.46  $\Delta H_{373} (\text{H}_2\text{O}(l)) = -284.11 \text{ kJ}$       Q.47  $24 \text{ kJ/mol}$

**Exercise-2**

|      |      |      |      |      |    |      |     |
|------|------|------|------|------|----|------|-----|
| Q.1  | D    | Q.2  | C    | Q.3  | B  | Q.4  | C   |
| Q.5  | C    | Q.6  | D    | Q.7  | B  | Q.8  | B   |
| Q.9  | C    | Q.10 | C    | Q.11 | C  | Q.12 | B   |
| Q.13 | B    | Q.14 | B    | Q.15 | C  | Q.16 | D   |
| Q.17 | A    | Q.18 | C    | Q.19 | B  | Q.20 | B   |
| Q.21 | D    | Q.22 | B    | Q.23 | C  | Q.24 | A   |
| Q.25 | B    | Q.26 | B    | Q.27 | C  |      |     |
| Q.28 | ABCD | Q.29 | ABCD | Q.30 | AD | Q.31 | ABD |
| Q.32 | D    | Q.33 | A    |      |    |      |     |

**EXERCISE-1 (Subjective Questions)****Rate of disappearance, Rate of appearance, Rate of Reactions**

- Q.1 Ammonia and oxygen reacts at higher temperatures as  

$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
 In an experiment, the concentration of NO increases by  $1.08 \times 10^{-2} \text{ mol litre}^{-1}$  in 3 seconds. Calculate.  
 (i) rate of reaction.  
 (ii) rate of disappearance of ammonia  
 (iii) rate of formation of steam
- Q.2 For the reaction :  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightarrow 2\text{NH}_{3(\text{g})}$ . If rate of appearance of  $\text{NH}_3$  is  $6.8 \times 10^{-3} \text{ gm/min}$ , then rate of disappearance of  $\text{H}_{2(\text{g})}$  at the same condition will be :
- Q.3 If the rate of decomposition of  $\text{N}_2\text{O}_5$  in the reaction,  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  at a particular instant is  $4.2 \times 10^{-7} \text{ M/s}$ . Then calculate -  
 (a) rate of reaction  
 (b) rate of appearance of  $\text{NO}_2$  and  $\text{O}_2$  at that instant.
- Q.4 Consider the chemical reaction balanced in two different ways.  

$$2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NOCl}(\text{g})$$
 and. 
$$\text{NO}(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NOCl}(\text{g})$$
 If rate of reaction according to first version is  $8 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$ . Then what is the rate of reaction according to second version.
- Q.5 The reaction,  $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NOCl}(\text{g})$  is carried out in a closed vessel. If partial pressure of NO is decreasing at rate of 180 torr/min. What is the rate of change of total pressure of vessel (in torr/s).
- Q.6 At  $27^\circ\text{C}$  it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of disappearance in  $\text{M sec}^{-1}$

**Rate Law**

- Q.7 For the elementary reaction :  

$$\text{H}_2\text{S}(\text{aq}) + \text{Cl}_2(\text{aq}) \rightarrow \text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$$
 The rate constant for disappearance of  $\text{H}_2\text{S}$  at  $25^\circ\text{C}$  is  $4 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ . If  $[\text{H}_2\text{S}] = 2 \times 10^{-4} \text{ M}$  and  $[\text{Cl}_2] = 0.025 \text{ M}$ . What is rate of formation of  $\text{Cl}^-$ ?
- Q.8 For the elementary reaction  $2\text{A} + \text{B}_2 \longrightarrow 2\text{AB}$ . Calculate how much the rate of reaction will change if  
 (a) the volume of the vessel is reduced to one third of its original volume?  
 (b) the volume of the vessel is doubled of its original volume?
- Q.9 The reaction  $\text{A}(\text{g}) + 2\text{B}(\text{g}) \longrightarrow \text{C}(\text{g}) + \text{D}(\text{g})$  is an elementary process. In an experiment, the initial partial pressure of A & B are  $P_A = 0.6$  and  $P_B = 0.8 \text{ atm}$ . Calculate the ratio of rate of reaction relative to initial rate when  $P_C$  becomes 0.2 atm.

**Zero Order**

- Q.10 In the following reaction:  $A \longrightarrow B$ , rate constant is  $1.2 \times 10^{-2} \text{ M s}^{-1}$ . What is concentration of B after 10 and 20 min., if we start with 10 M of A.
- Q.11 A zero order reaction :  $X \rightarrow Y$ . At the end of 50 min, X is 75% reacted. How much of it will be left unreacted at the end of 2 hour.
- Q.12 The initial rate of zero order reaction of a gaseous reaction,  

$$A(g) \longrightarrow 2B(g),$$
 is  $10^{-3} \text{ M min}^{-1}$ . If initial concentration of A is 2M. Then what would be rate of reaction after 120 seconds.
- Q.13 For the following data for the zero order reaction  $A \longrightarrow$  products. Calculate the value of k.
- | Time (min.) | [A]    |
|-------------|--------|
| 0.0         | 0.10 M |
| 1.0         | 0.09 M |
| 2.0         | 0.08 M |
- Q.14 Decomposition of reaction :  

$$2A(g) \longrightarrow 2B(g) + C(g)$$
 Follows zero order kinetics. Initial rate of decomposition of A is 0.1 atm/s. If initially A is taken at 2 atm pressure then what will be rate of reaction after 10 seconds.
- Q.15 The rate constant for a zero order reaction is  $2 \times 10^{-2} \text{ mol L}^{-1} \text{ sec}^{-1}$ , if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.
- Q.16 A drop of solution (volume 0.10 ml) contains  $6 \times 10^{-6}$  mole of  $H^+$ , if the rate constant of disappearance of  $H^+$  is  $1 \times 10^7 \text{ mol L}^{-1} \text{ s}^{-1}$ . How long would it take for  $H^+$  in drop to disappear?
- Q.17 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

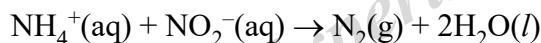
**First Order**

- Q.18 A first order reaction is 75% completed in 72 min.. How long time will it take for  
 (i) 50% completion (ii) 87.5% completion  
 (iii) Fraction of reactant left after 108 min
- Q.19 A first order reaction is 20% complete in 10 min. calculate  
 (i) the specific rate of reaction ,  
 (ii) the time taken for the reactions to go to 75% completion.  
 (iii) Fraction of reactant decompsed after 40 min
- Q.20 The rate constant for an isomerisation reaction  $A \rightarrow B$  is  $4.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h.
- Q.21 The rate of a first order reaction is  $0.04 \text{ mole L}^{-1} \text{ s}^{-1}$  at 10 minutes and  $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$  at 20 minutes after initiation. Find the half life of the reaction.

- Q.22 In the first order decomposition of A :  $A \rightarrow 2B + 3C$   
Concentration of A decrease from initial concentration 0.8M to 0.2M in 13.86 min. then calculate rate of appearance of B (in M/s) after 13.86 min.
- Q.23 For a 1<sup>st</sup> order reaction :  $A \rightarrow 3B + 2C$ , with initial concentration 2M of A, it is 20% completed in 50 min. If initial concentration of A = 10M, then find the concentration of B after 50 min.
- Q.24 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0 % of the virus was found to be inactivated per minute . Evaluate k (in s<sup>-1</sup>) for inactivation process.  
**Given :**  $\ln\left(\frac{100}{98}\right) = 0.02$
- Q.25 The reaction  $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$  is a first order gas reaction with  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$  at 320°C. What % of  $\text{SO}_2\text{Cl}_2$  is decomposed on heating this gas for 90 min.  
**Given :**  $e^{-0.1188} = 0.888$
- Q.26 For a first order reaction :  $A \rightarrow \text{Product}$  the concentration of A changes 2 M to 0.5 M in 4 min. Then calculate rate of reaction(M s<sup>-1</sup>) after 6 min. [ $\ln 2 = 0.7$ ]
- Q.27 Decomposition of 1 L  $\text{H}_2\text{O}_2$  follows a first order reaction. In 46 minutes the concentration of  $\text{H}_2\text{O}_2$  decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of  $\text{H}_2\text{O}_2$  reaches 0.05 M, then calculate of rate of formation of  $\text{O}_2$  (in mol s<sup>-1</sup>). ( $\ln 2 = 0.69$ ):
- Q.28 The half-life for first order decomposition of  $\text{N}_2\text{O}_4$  is  $1.4 \times 10^{-5} \text{ s}$ .  
 $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$   
If  $\text{N}_2\text{O}_4$  is introduced into an evacuated flask at a pressure of 20mm Hg, how many seconds are required for pressure of  $\text{NO}_2$  to reach 10 mm Hg?
- Q.29 At 500°C, cyclopropane( $\text{C}_3\text{H}_6$ ) rearranges to propene ( $\text{CH}_3\text{—CH=CH}_2$ ). The reaction is first order and the rate constant is  $4 \times 10^{-3} \text{ s}^{-1}$ . If initial concentration of cyclopropane  $\text{C}_3\text{H}_6$  is 0.05M.  
[**Given :**  $\ln 5 = 1.6$ ,  $\ln 2 = 0.7$ ]  
Then  
(a) What is molarity of cyclopropane  $\text{C}_3\text{H}_6$  after  $\frac{20}{3}$  min?  
(b) How many minutes does it take for  $\text{C}_3\text{H}_6$  concentration to drop to 0.01 M.  
(c) After how many minutes 20% of cyclopropane will be left.
- Q.30 The gas phase reaction :  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$   
is found to be first order. The reaction was carried out at constant temperature of 340K in a constant volume container. The initial pressure is equal to 0.1 bar and no substance is initially present except for  $\text{N}_2\text{O}_5$ . The total pressure was 0.16 bar after 100 sec of reaction. Calculate  
[**Given :**  $\ln 10 = 2.3$ ,  $\ln 6 = 1.8$ ,  $\ln 2 = 0.7$ ]  
(a) value of rate constant.  
(b) partial pressure of  $\text{N}_2\text{O}_5$  after 100 sec of reaction.  
(c) half life ( $t_{1/2}$ )

Order of Reaction & Rate law

Q.31 Initial rate data at 25°C are listed in the table for reaction.



| Experiment | Initial<br>[NH <sub>4</sub> <sup>+</sup> ] | Initial<br>[NO <sub>2</sub> <sup>-</sup> ] | Initial rate of consumption<br>of [NH <sub>4</sub> <sup>+</sup> ] (M/s) |
|------------|--------------------------------------------|--------------------------------------------|-------------------------------------------------------------------------|
| 1          | 0.24                                       | 0.1                                        | $7.2 \times 10^{-6}$                                                    |
| 2          | 0.12                                       | 0.1                                        | $3.6 \times 10^{-6}$                                                    |
| 3          | 0.12                                       | 0.15                                       | $5.4 \times 10^{-6}$                                                    |

(a) What is the rate law ?

(b) What is the value of rate constant ?

(c) What is initial rate when initial concentration are [NH<sub>4</sub><sup>+</sup>] = 0.4 M and [NO<sub>2</sub><sup>-</sup>] = 0.5 M ?

Q.32 The following result have been obtained during kinetic studies of the reaction.



| Experiment | [A]/M | [B]/M | Initial rate of formation<br>of D / M s <sup>-1</sup> |
|------------|-------|-------|-------------------------------------------------------|
| I          | 0.1   | 0.1   | $6.0 \times 10^{-3}$                                  |
| II         | 0.3   | 0.2   | $7.2 \times 10^{-2}$                                  |
| III        | 0.3   | 0.4   | $2.88 \times 10^{-1}$                                 |
| IV         | 0.4   | 0.1   | $2.40 \times 10^{-2}$                                 |

(a) Determine the rate law of above reaction

(b) Find the rate constant of above reaction in (mol/L)<sup>1-n</sup> s<sup>-1</sup>

Q.33 The following data is obtained for the reaction :  $\text{A}_{(\text{aq})} \longrightarrow 2\text{B}_{(\text{aq})} + \text{C}_{(\text{aq})}$

| Time (min)           | 0   | 20   | 40    | 60     |
|----------------------|-----|------|-------|--------|
| Concentration of 'A' | 0.1 | 0.09 | 0.081 | 0.0729 |

Then calculate order of reaction :

Q.34 For the reaction :  $\text{A} \longrightarrow \text{Products}$ , the time for 75% completion of reaction is 5 times the time for 50% completion of reaction. Then calculate order of reaction.

Q.35 For a gaseous reaction :  $2\text{A}_{(\text{g})} \longrightarrow 3\text{B}_{(\text{g})} + 4\text{C}_{(\text{g})}$  occurring in a rigid vessel, if initially pressure is 3 atm and after 10 minutes & 20 minutes the pressure is 6.75 atm and 10.5 atm respectively, then what will be the order of reaction?

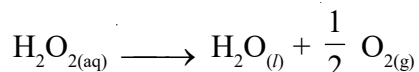
Q.36 At 300 K, the rate of decomposition of a gaseous compound initially at a pressure of 20 kPa was 13.5 Pa s<sup>-1</sup> when 10% had reacted and 0.5 Pa s<sup>-1</sup> when 70% had reacted. Then Calculate order of reaction is :

Calculation of Rate Constant using Different Parameters

- Q.37 The reaction  $\text{AsH}_3(\text{g}) \longrightarrow \text{As}(\text{s}) + \frac{3}{2} \text{H}_2(\text{g})$  was followed at constant volume at  $310^\circ\text{C}$  by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.

|                        |     |     |     |     |
|------------------------|-----|-----|-----|-----|
| Time (in hrs)          | 0   | 5   | 7.5 | 10  |
| Total pressure (in mm) | 758 | 827 | 856 | 882 |

- Q.38 The decomposition of  $\text{H}_2\text{O}_2$  follows first order kinetics :



In order to determine the rate constant of reaction, a definite volume of reaction mixture is titrated with standard  $\text{KMnO}_4$  solution, at different time. What is the value of 'X' in the following data?

|                           |    |    |    |
|---------------------------|----|----|----|
| Time(min)                 | 0  | 10 | 20 |
| Volume of $\text{KMnO}_4$ | 25 | 20 | X  |

- Q.39 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction



at  $500^\circ\text{C}$  is as follows:

|                           |     |      |      |          |
|---------------------------|-----|------|------|----------|
| Time (s)                  | 390 | 1195 | 3155 | $\infty$ |
| Pressure increase (mm Hg) | 96  | 250  | 467  | 624      |

the initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant of reaction.

- Q.40 The polarimeter readings in an experiment to measure the rate of inversion of cane sugar (1<sup>st</sup> order) were as follows.

|                          |            |            |             |
|--------------------------|------------|------------|-------------|
| Time (min)               | 0          | 30         | $\infty$    |
| Rotation due to solution | $60^\circ$ | $40^\circ$ | $-30^\circ$ |

Which of the following is / are correct : [Given :  $\log 2 = 0.3$ ,  $\log 3 = 0.48$ ,  $\log 7 = 0.84$ ,  $\log_e 10 = 2.3$ ]

- (a) The half life( $t_{1/2}$ ) of reaction  
(b) The time at which solution becomes optically inactive.

- Q.41  $\text{A} \xrightarrow{1^{\text{st}} \text{ order}} \text{B} + \text{C}$

|                         |       |          |
|-------------------------|-------|----------|
| Time                    | t     | $\infty$ |
| Total pressure of (B+C) | $P_2$ | $P_3$    |
| Find k.                 |       |          |

- Q.42  $\text{S} \xrightarrow{1^{\text{st}} \text{ order}} \text{G} + \text{F}$

|                                |       |            |
|--------------------------------|-------|------------|
| Time                           | t     | $\infty$   |
| Rotation of Glucose & Fructose | $r_t$ | $r_\infty$ |
| Find k.                        |       |            |



- Q.43 The following data were obtained in experiment on inversion of cane sugar.
- |                            |       |       |       |      |       |          |
|----------------------------|-------|-------|-------|------|-------|----------|
| Time (min)                 | 0     | 60    | 120   | 180  | 360   | $\infty$ |
| Angle of rotation (degree) | +13.1 | +11.6 | +10.2 | +9.0 | +5.87 | -3.8     |
- Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?
- Q.44 At 100°C the gaseous reaction  $A \longrightarrow 2B + C$  was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find
- initial pressure of A
  - the pressure of A at the end of 10 minutes
  - the specific rate of reaction
  - the half life period of the reaction? [Given :  $\ln\left(\frac{90}{47}\right) = 0.65n$ ]
- Q.45 The decomposition of  $N_2O_5$  according to the equation  $2 N_2O_5(g) \longrightarrow 4 NO_2(g) + O_2(g)$  is a first order reaction. After 30 min. from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction. [Given :  $\ln 1.169 = 0.156$ ]
- Q.46 Decomposition of reaction  $3A(g) \longrightarrow 2B(g) + 2C(g)$  follows first order kinetics. Starting with pure 'A' pressure developed after 20 min. and infinite time are 3.5 atm and 4 atm respectively. What is the time (in minutes) taken for 75 % decomposition of A?
- Q.47 For a reaction :  $2A_{(g)} \rightarrow 3B_{(g)} + C_{(g)}$  the pressure at different instants is given as shown :

|                     |    |       |          |
|---------------------|----|-------|----------|
| Time(min)           | 0  | 13.86 | $\infty$ |
| Total pressure (mm) | 50 | 80    | 90       |

Calculate value of rate constant in  $\text{min}^{-1}$  ? [Given :  $\ln 2 = 0.693$ ]

- Q.48 Acid catalysed hydrolysis of  $\text{CH}_3\text{COOC}_2\text{H}_5$  is monitored by taking equal amount of solution after certain interval of time and titrating it with NaOH. Following data were obtained.

$$\text{Rate} = K [\text{H}^+] [\text{CH}_3\text{COOC}_2\text{H}_5]$$

|                       |    |    |          |
|-----------------------|----|----|----------|
| Time(min)             | 0  | 20 | $\infty$ |
| Volume of NaOH(in ml) | 20 | 80 | 100      |

If  $[\text{H}^+] = 0.7 \text{ M}$ . Find 'K' in  $\text{M}^{-1} \text{ s}^{-1}$ . [Take :  $\ln 2 = 0.7$ ]

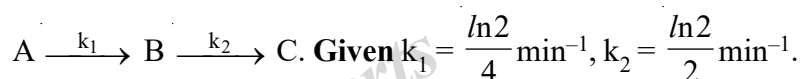
- Q.49 The reaction  $A(\text{aq}) \longrightarrow B(\text{aq}) + C(\text{aq})$  is monitored by measuring optical rotation of reaction mixture at different time interval. The species A, B and C are optically active with specific rotations  $20^\circ$ ,  $30^\circ$  and  $-40^\circ$  respectively. Starting with pure A if the value of optical rotation was found to be  $2.5^\circ$  after 6.93 minutes and optical rotation was  $-5^\circ$  after infinite time. Find the rate constant for first order conversion of A into B and C.

Parallel and Sequential Reaction

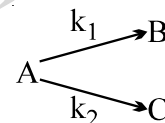
Q.50 For a reaction  $x \begin{cases} \xrightarrow{k_1} y \\ \xrightarrow{k_2} z \end{cases}$ , calculate value of ratio,  $\frac{[x]_t}{[y] + [z]}$  at any given instant t.

Q.51  $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$   $k_1 = x \text{ hr}^{-1}$ ;  $k_1 : k_2 = 1 : 10$ . Calculate  $\frac{[C]}{[A]}$  after one hour from the start of the reaction.  
Assuming only A was present in the beginning.

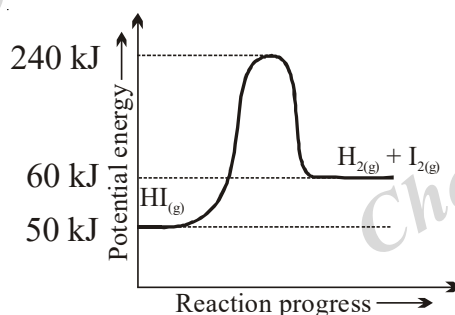
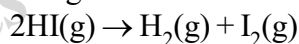
Q.52 How much time would be required for the B to reach maximum concentration for the reaction



Q.53 For first order parallel reaction  $k_1$  and  $k_2$  are 8 and  $2 \text{ min}^{-1}$  respectively at 300 K. If the activation energies for the formation of B and C are respectively 20 and 28.314 kJ/mol respectively find the temperature at which B and C will be obtained in molar ratio of 2 : 1.  
[Given :  $\ln 4 = 1.4$ ]

Temperature Dependence of Rate (Activation Energy)

Q.54 Potential energy profile for a reaction is given as :

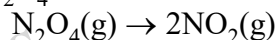


- Calculate activation energy for forward reaction and backward reaction respectively.
- Calculate  $\Delta E$  of reaction :
- Is reaction endothermic or exothermic?
- Fraction of molecules having sufficient kinetic energy to cross threshold barrier at 300K.

[Given  $R = \frac{25}{3} \text{ J / K - mol}$ ]

Q.55 What fraction of molecules in a gas at 300 K collide with an energy equal to or greater than  $E_a$  when  $E_a$  equals 50 kJ/mol. [Given :  $R = \frac{25}{3} \text{ J / mol-K}$ ]

- Q.56 The gas phase decomposition of  $\text{N}_2\text{O}_4$  is a first order reaction :



Use the following data to calculate activation energy. [in KCal /mol]

[Given :  $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ]

| Temperature[°C] | Initial $[\text{N}_2\text{O}_4]$ | Initial rate of decomposition<br>of $\text{N}_2\text{O}_4$ (M/s) |
|-----------------|----------------------------------|------------------------------------------------------------------|
| 27              | 0.1                              | $5 \times 10^3$                                                  |
| 47              | 0.15                             | $2 \times 10^4$                                                  |

- Q.57 Rate constants for the reaction :  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$  are  $1.3 \text{ M}^{-1}\text{s}^{-1}$  at 600K and  $26 \text{ M}^{-1}\text{s}^{-1}$  at 800K. [Given :  $\ln 10 = 2.3$ ,  $\ln 2 = 0.7$ ]

Calculate :

- (a) activation energy in KCal /mol. (b) rate constant at 1200K.

- Q.58 If rate of reaction increases by a factor of 2, when temperature is raised from 27°C to 37°C. What is the value of activation energy in kJ/mol? By what factor does rate of reaction increase if temperature is increased from 127°C to 137°C.

[Given :  $\ln 2 = 0.7$ ,  $R = 8.314 \text{ Joule/mol-K}$ ,  $e^{0.4} = 1.5$ ]

- (a) If temperature coefficient ( $\mu$ ) is same in given temperature range  
(b) If temperature coefficient ( $\mu$ ) is function of temperature.

- Q.59 The dependence of rate constant of a reaction on temperature may be given as :

$$\ln K [\text{sec}^{-1}] = 12.5 - \frac{500}{T(\text{K})}$$

Calculate the activation energy of reaction(in Cal/mol).

- Q.60 A catalyst lowers the activation energy for a certain reaction from  $75 \text{ Kcal mol}^{-1}$  to  $15 \text{ Kcal mol}^{-1}$ . What will be the effect on the rate of reaction at 27°C, other things being equal.

- Q.61 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate at 25°C.

- Q.62 75 % of a first order reaction occurs in 30 min at 27°C. 87.5 % of the same reaction occurs in 30 min at 57°C. The activation energy of reaction is [ $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ]

- Q.63 The Arrhenius equation for two first order equation

$\text{A} \longrightarrow \text{B}$  and  $\text{C} \longrightarrow \text{D}$  is given by

$$k_1 = 10^{12} e^{-81.28(\text{kJ})/\text{RT}}; \quad k_2 = 10^{11} e^{-43.10(\text{kJ})/\text{RT}}$$

At what temperature  $k_1$  becomes equal to  $k_2$ . The unit of activation energy is kJ/mol

Use:  $\ln 10 = 2.3$  and  $R = 8.3 \text{ J/K/mol}$

- Q.64 At room temperature 300 K orange juice gets spoilt in about 52 hours. In a refrigerator at 200 K juice can be stored three times as long before it gets spoilt. Estimate

- (a) the activation energy of the reaction that causes the spoiling of juice.  
(b) How long should it take for juice to get spoilt at 400 K ?

Given :  $\ln 3 = 1.1$ ,  $e^{(11/20)} = 1.733$

- Q.65 The rate of reaction :  $A_{(g)} \rightarrow 2B_{(g)}$  increases  $e^5$  times on increasing the temperature from  $27^\circ\text{C}$  to  $327^\circ\text{C}$ . The activation energy (in Kcal/mol) of reaction is :  
[Assuming activation energy is temperature independent]
- Q.66 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by  $20 \text{ kJmol}^{-1}$ .
- Q.67 For the system  $A(g) \rightleftharpoons B(g)$ ,  $\Delta H$  for the forward reaction is  $-3000R$  (Note :  $\Delta H = \Delta E$  in this case). Show that equilibrium constant  $K = \frac{[B]}{[A]} = e^{10}$  at 300 K. If the activation energies  $E_f$  &  $E_b$  are in the ratio 12 : 17, calculate  $E_f$  and  $E_b$  at this temperature. Assume that the pre-exponential factor is the same for the forward and backward reactions.

### Mechanism of Reaction

- Q.68 The reaction  $2\text{NO} + \text{Br}_2 \longrightarrow 2\text{NOBr}$ , is supposed to follow the following mechanism  
(i)  $\text{NO} + \text{Br}_2 \xrightleftharpoons{\text{fast}} \text{NOBr}_2$   
(ii)  $\text{NOBr}_2 + \text{NO} \xrightarrow{\text{slow}} 2\text{NOBr}$   
Suggest the rate law expression.
- Q.69 For the reaction  $2\text{H}_2 + 2\text{NO} \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ , the following mechanism has been suggested:  
 $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$  equilibrium constant  $K_1$  (fast)  
 $\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O}$  (slow)  
 $\text{N}_2\text{O} + \text{H}_2 \xrightarrow{k_3} \text{N}_2 + \text{H}_2\text{O}$  (fast)  
Establish the rate law for given reaction.
- Q.70 Reaction between NO and  $\text{O}_2$  to form  $\text{NO}_2$  is  $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$  follows the following mechanism  
 $\text{NO} + \text{NO} \xrightleftharpoons[k_{-1}]{k_1} \text{N}_2\text{O}_2$  (in rapid equilibrium)  
 $\text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_2} 2\text{NO}_2$  (slow)

Show that the rate of reaction is given by

$$\frac{1}{2} \left( \frac{d[\text{NO}_2]}{dt} \right) = K[\text{NO}]^2[\text{O}_2]$$

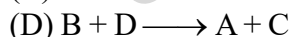
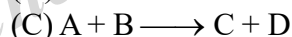
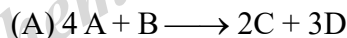
## EXERCISE-2 (Objective Questions)

Single correct

Q.1 The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:



Q.2 For the reaction :  $2NO_{2(g)} \rightarrow 2NO_{(g)} + O_{2(g)}$  at a certain temperature, the initial rate of decomposition of  $NO_2$  is  $0.0036 \text{ Ms}^{-1}$ . What is initial rate of formation of  $O_2(g)$  in  $\text{Mmin}^{-1}$ ?

(A) 0.0018

(B) 0.0108

(C) 0.108

(D) 0.0072

Q.3 The gas phase decomposition of dinitrogen pentoxide is represented by this equation:



What is rate of formation of oxygen gas (in  $\text{mol L}^{-1} \text{ s}^{-1}$ ) in an experiment where 0.08 mol of  $N_2O_5$  is consumed in a 4L container every 0.2 seconds?

(A) 0.02

(B) 0.05

(C) 0.1

(D) 0.2

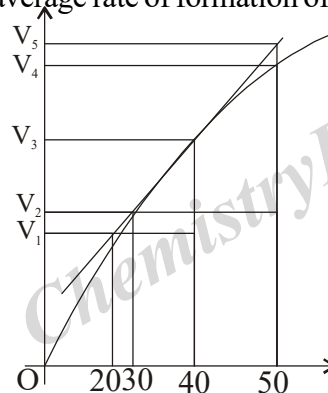
Q.4 A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in figure. On the basis of this mark the correct option for average rate of formation of  $H_2$  gas.

(A) Average rate upto 40 s is  $\frac{V_3 - V_2}{40}$

(B) Average rate upto 40 s is  $\frac{V_3 - V_2}{40 - 30}$

(C) Average rate upto 40 s is  $\frac{V_3}{40}$

(D) Average rate upto 40 s is  $\frac{V_3 - V_1}{40 - 20}$



Q.5 Consider the graph given in **above figure**. Which of the following options does not show instantaneous rate of formation of  $H_2$  gas at 40<sup>th</sup> second?

(A)  $\frac{V_5 - V_2}{50 - 30}$

(B)  $\frac{V_4 - V_2}{50 - 30}$

(C)  $\frac{V_3 - V_2}{40 - 30}$

(D)  $\frac{V_3 - V_1}{40 - 20}$

Q.6 The rate of formation  $O_3(g)$  is  $96 \times 10^{-7} \text{ gL}^{-1} \text{ s}^{-1}$  for the reaction.:  $3O_2(g) \rightarrow 2O_3(g)$  What is rate of disappearance of  $O_2(g)$  in  $\text{mol L}^{-1} \text{ s}^{-1}$ ?

(A)  $96 \times 10^{-7}$

(B)  $1.5 \times 10^{-7}$

(C)  $3 \times 10^{-7}$

(D)  $0.66 \times 10^{-7}$

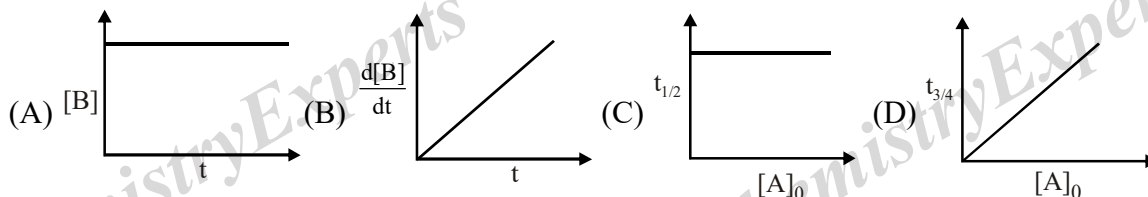
- Q.7 The rate law for a reaction between the substances A and B is given by  

$$\text{rate} = k [A]^n [B]^m$$
 On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as  
 (A)  $2^{(n-m)}$  (B)  $1/2^{(m+n)}$  (C)  $(m+n)$  (D)  $(n-m)$
- Q.8 The rate of the simple reaction  $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ , when the volume of the reaction vessel is doubled.  
 (A) Will grow eight times of its initial rate (B) Reduce to one-eight of its initial rate  
 (C) Will grow four times of its initial rate (D) Reduce to one-fourth of its initial rate
- Q.9 The rate of a stoichiometric/elementary reaction between a solid and a gas in a container may be increased by increasing all of the following factors except the \_\_\_\_\_  
 (A) pressure of gas (B) temperature of gas  
 (C) volume of container (D) surface area of solid
- Q.10 Consider a first order reaction at 300 K, started with initial partial pressure of A 20 torr and no other gas.  

$$\text{A(g)} \longrightarrow \text{B(g)} + 2\text{C(g)}$$
 After 10 sec. total pressure of gaseous mixture was 40 torr.  
 Determine rate constant for above reaction with the help of following data :  
 [Take :  $\ln 2 = 0.7$ ]  
 (A)  $0.7 \text{ sec}^{-1}$  (B)  $0.07 \text{ sec}^{-1}$  (C)  $0.05 \text{ sec}^{-1}$  (D)  $0.14 \text{ sec}^{-1}$
- Q.11 For first order decomposition,  

$$\text{A} \longrightarrow 2\text{B} + 3\text{C}$$
 Concentration of A decreases from 1 M to 0.7 M in 10 seconds. What would be the concentration of A left after next 20 seconds.  
 (A) 0.1 M (B) 0.147 M (C) 0.21 M (D) 0.343
- Q.12 In a first order reaction, the concentration of the reactant, decreases from 0.8 to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is  
 (A) 30 minutes (B) 15 minutes (C) 7.5 minutes (D) 60 minutes
- Q.13 The rate equation for the reaction  $2\text{A} + \text{B} \longrightarrow \text{C}$  is found to be :  $\text{rate} = k [\text{A}] [\text{B}]$ . The correct statement in relation to this reaction is  
 (A) unit of k must be  $\text{s}^{-1}$   
 (B)  $t_{1/2}$  is a constant  
 (C) rate of formation of C is twice the rate of disappearance of A  
 (D) value of k is independent of the initial concentrations of A and B.
- Q.14  $t_{1/4}$  can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its value. If the rate constant for a first order reaction is k, the  $t_{1/4}$  can be written as [ $\ln 2 = 0.695$ ,  $\ln 3 = 1.1$ ]  
 (A)  $0.69 / k$  (B)  $0.75 / k$  (C)  $0.10 / k$  (D)  $0.29 / k$

Q.15 Which graph represents zero order reaction  $[A(g) \rightarrow B(g)]$  :



Q.16 Consider a first order reaction at 300 K, started with initial partial pressure of A 20 torr and no other gas.  $A(g) \longrightarrow B(g) + 2C(g)$

After 10 sec. total pressure of gaseous mixture was 40 torr. Determine rate constant for above reaction with the help of following data : [Take :  $\ln 2 = 0.7$ ]

- (A)  $0.7 \text{ sec}^{-1}$  (B)  $0.07 \text{ sec}^{-1}$  (C)  $0.05 \text{ sec}^{-1}$  (D)  $0.14 \text{ sec}^{-1}$

Q.17 Consider the following reaction  $2A(g) \rightarrow 3B(g) + C(g)$ .

Starting with pure A having pressure 2 atm initially, the total pressure is exactly doubled in 2 hrs. The possible order of reaction is

- (A) zero (B) first (C) second (D) third

Q.18 Decomposition of reaction :  $2A(g) \longrightarrow 2B(g) + C(g)$

Follows zero order kinetics. Initial rate of decomposition of A is  $0.1 \text{ atm/sec}$ . If initially A is taken at 2 atm pressure then what will be rate of reaction after 10 seconds.

- (A)  $0.1 \text{ atm/sec}$  (B)  $0.05 \text{ atm/sec}$  (C) zero (D)  $0.5 \text{ atm/sec}$

Q.19 The rate constant for the dissociation of  $N_2O_5$  :  $2N_2O_5 \longrightarrow 4NO_2 + O_2$  is  $3.0 \times 10^{-5} \text{ sec}^{-1}$ . If the rate is  $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$ , then the concentration of  $N_2O_5$  (in  $\text{mol litre}^{-1}$ ) is

- (A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8

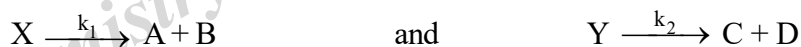
Q.20 For a reaction :  $2A_{(g)} \rightarrow B_{(g)} + 3C_{(g)}$ , rate constant of disappearance of A is  $10^{-3} \text{ M s}^{-1}$ . If initially 2M of A is taken then what will be concentration of C after 5 minutes.

- (A) 0.3 M (B) 0.9 M (C) 0.45 M (D)  $1.5 \times 10^{-2} \text{ M}$

Q.21 The initial rate of zero order reaction of the gaseous reaction  $A(g) \longrightarrow 2B(g)$  is  $10^{-2} \text{ M min}^{-1}$ . If the initial concentration of A is 0.1 M, after 60 s concentration of B would be

- (A) 0.09 M (B) 0.01 M (C) 0.02 M (D) 0.002 M

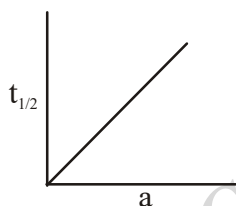
Q.22 Consider the following first order competing reactions:



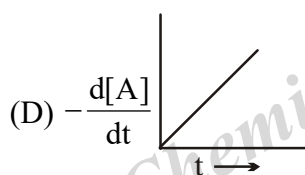
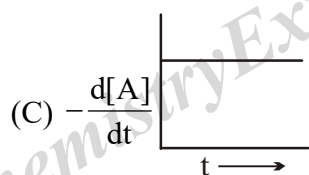
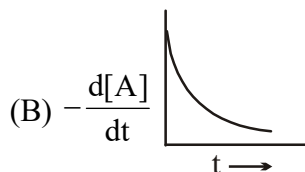
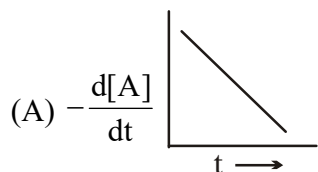
if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants ( $k_2/k_1$ ) is

- (A) 4.06 (B) 0.215 (C) 1.1 (D) 4.65

- Q.23 Consider the reaction  $A \longrightarrow B$ , graph between half life ( $t_{1/2}$ ) and initial concentration (a) of the reactant is



Hence graph between  $-\frac{d[A]}{dt}$  and time will be



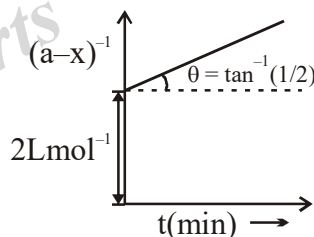
- Q.24 At certain temperature, the half life period for the thermal decomposition of a gaseous substance depends on the initial partial pressure of the substance as follows

|                     |     |     |
|---------------------|-----|-----|
| P(mmHg)             | 500 | 250 |
| $t_{1/2}$ (in min.) | 235 | 940 |

Find the order of reaction

- (A) 1 (B) 2 (C) 2.5 (D) 3
- Q.25 For a reaction  $A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$ , the rate constant for the reaction is  $3 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$ . At what concentration of A will the rate of reaction be  $2 \times 10^{-3} \text{ M min}^{-1}$ .
- (A) 1 M (B) 0.52 M (C) 0.82 M (D)  $\frac{2}{3} \text{ M}$

- Q.26 From the following graph between  $(a-x)^{-1}$  and time 't' for a reaction, calculate rate of disappearance at the start of the reaction.

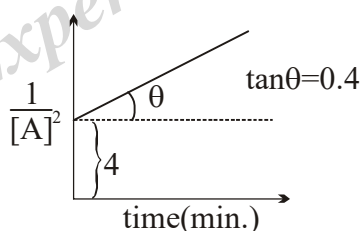


- (A)  $1.25 \text{ mol L}^{-1} \text{ min}^{-1}$   
(C)  $0.25 \text{ mol L}^{-1} \text{ min}^{-1}$

- (B)  $0.5 \text{ mol L}^{-1} \text{ min}^{-1}$   
(D)  $0.125 \text{ mol L}^{-1} \text{ min}^{-1}$

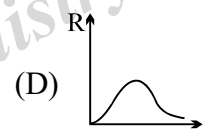
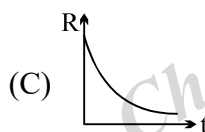
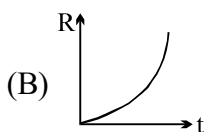
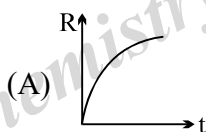


- Q.27 For a reaction **A**  $\rightarrow$  **Product**, a graph plotted between  $\frac{1}{[A]^2}$  vs time is found to be linear with slope = 0.4 and y intercept equal to 4 as shown. The rate of disappearance of **A** at the initial stages will be :

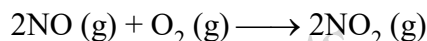


[A] is in terms of molarity

- (A) 0.025 M/s  
(B)  $4.16 \times 10^{-4}$  M/s  
(C) 1.6 M/s  
(D) 0.8 M/s
- Q.28 If decomposition reaction  $A(g) \rightarrow B(g)$  follows first order kinetics then the graph of rate of formation (R) of B against time t will be



- Q.29 For reaction,



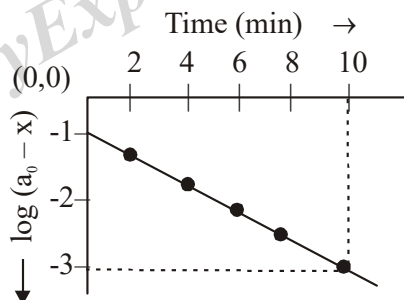
Rate law is : rate of reaction =  $K [NO]^2 [O_2]$

When  $[NO] = 0.04$  M and  $[O_2] = 0.02$  M, the rate of disappearance of NO is  $3.2 \times 10^{-5}$  M/s.

Then value of  $K'$  in

$$-\frac{d[O_2]}{dt} = K' [NO]^2 [O_2]$$

- (A)  $0.5 \text{ min}^{-1} \text{ M}^{-2}$   
(B)  $30 \text{ min}^{-1} \text{ M}^{-2}$   
(C)  $8.33 \times 10^{-3} \text{ min}^{-1} \text{ M}^{-2}$   
(D)  $30 \text{ min}^{-1} \text{ M}^{-1}$
- Q.30 For the first order decomposition of  $SO_2Cl_2(g)$ ,  
 $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$   
 a graph of  $\log(a_0 - x)$  vs t is shown in figure. What is the rate constant ( $s^{-1}$ )?



- (A) 0.2  
(B)  $4.6 \times 10^{-1}$   
(C)  $7.7 \times 10^{-3}$   
(D)  $1.15 \times 10^{-2}$

- Q.31 Reaction  $A + B \longrightarrow C + D$  follows following rate law :  $\text{rate} = k[A]^{\frac{1}{2}}[B]^{\frac{1}{2}}$ . Starting with initial conc. of 1 M of A and B each, what is the time taken for concentration of A to become 0.25 M.  
Given :  $k = 2.303 \times 10^{-3} \text{ s}^{-1}$ .  
(A) 300 s (B) 600 s (C) 900 s (D) 1200 s
- Q.32 In a first order reaction the concentration of reactant decreases from  $800 \text{ mol/dm}^3$  to  $50 \text{ mol/dm}^3$  in  $2 \times 10^4 \text{ s}$ . The rate constant of reaction in  $\text{s}^{-1}$  is  
(A)  $2 \times 10^4$  (B)  $3.45 \times 10^{-5}$  (C)  $1.3864 \times 10^{-4}$  (D)  $2 \times 10^{-4}$
- Q.33 Units of rate constant for the first and zero order reactions in terms of molarity, M units are respectively  
(A)  $\text{s}^{-1}, \text{M s}^{-1}$  (B)  $\text{s}^{-1}, \text{M}$  (C)  $\text{M s}^{-1}, \text{s}^{-1}$  (D)  $\text{M}, \text{s}^{-1}$
- Q.34 For a zero order reaction and a 1<sup>st</sup> order reaction half life are in ratio of 4 : 1. Calculate ratio of time taken to complete 87.5 % reaction for zero order : first order reaction respectively.  
(A) 7 : 3 (B) 3 : 7 (C) 4 : 1 (D) 5 : 3
- Q.35 For first order isomerisation reaction :  $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$   
How do the properties of the reaction in the table below vary as reaction proceeds?

|     | Rate of reaction $-\frac{\Delta[\text{CH}_3\text{NC}]}{\Delta t} (\text{M.s}^{-1})$ | Half life(s)    |
|-----|-------------------------------------------------------------------------------------|-----------------|
| (a) | Remain the same                                                                     | Decreases       |
| (b) | Decreases                                                                           | Remain the same |
| (c) | Remain the same                                                                     | Remain the same |
| (d) | Decreases                                                                           | Decreases       |

- (A) (a) (B) (b) (C) (c) (D) (d)

- Q.36 At 1800 K ethane gas decomposes to ethene and hydrogen. Rate constant for the reaction is  $10^{-3} \text{ Pa}^{-1} \text{ sec}^{-1}$ . If initial pressure of ethane is  $3 \times 10^5 \text{ Pa}$ , how many sec. would it take for the pressure to reach  $5 \times 10^5 \text{ Pa}$ ?  
(A) 1800.2 sec. (B)  $3.33 \times 10^{-2} \text{ sec.}$  (C)  $6.66 \times 10^{-3} \text{ sec.}$  (D) 1000.4 sec.
- Q.37 The formation of oxide layer on metals follows first order kinetics and completely stops when the oxide thickness becomes 10 nm. If one hour after exposure of oxygen to metal surface the thickness is 7.5 nm, then what would be the thickness 120 minute after the exposure?  
(A) 10 nm (B) 5.25 nm (C) 8.475 nm (D) 9.375 nm
- Q.38 For the reaction :  $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$   
Following data is given :

| S.No. | [CO](mol/L) | O <sub>2</sub> (mol/L) | Rate(mol/L – min)  |
|-------|-------------|------------------------|--------------------|
| 1.    | 0.02        | 0.02                   | $4 \times 10^{-5}$ |
| 2.    | 0.04        | 0.02                   | $8 \times 10^{-5}$ |
| 3.    | 0.02        | 0.04                   | $2 \times 10^{-5}$ |

The overall order of reaction is -

- (A) 0 (B) 1 (C) 2 (D) -1

- Q.39 For the reaction  $A + B \longrightarrow C$ ; starting with different initial concentration of A and B, initial rate of reaction were determined graphically in four experiments.

| S.No. | [A] <sub>0</sub> /M (Initial conc.) | [B] <sub>0</sub> /M (Initial conc.) | rate/(M sec <sup>-1</sup> ) |
|-------|-------------------------------------|-------------------------------------|-----------------------------|
| 1     | $1.6 \times 10^{-3}$                | $5 \times 10^{-2}$                  | $10^{-3}$                   |
| 2     | $3.2 \times 10^{-3}$                | $5 \times 10^{-2}$                  | $4 \times 10^{-3}$          |
| 3     | $1.6 \times 10^{-3}$                | $10^{-1}$                           | $2 \times 10^{-3}$          |
| 4     | $3.2 \times 10^{-3}$                | $10^{-1}$                           | $8 \times 10^{-3}$          |

Rate law for reaction from above data is

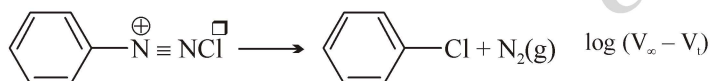
- (A)  $r = k[A]^2[B]^2$  (B)  $r = k[A]^2[B]$  (C)  $r = k[A][B]^2$  (D)  $r = k[A][B]$

- Q.40 For an elementary reaction :  $2A(g) \rightarrow B(g) + 2C(g)$

If initial pressure of A(g) is 20 torr and after 20 seconds, total pressure becomes 25 torr. Then after this point how long would it take total pressure to increase to 27.5 torr.

- (A) 40 s (B) 60 s (C) 30 s (D) 50 s

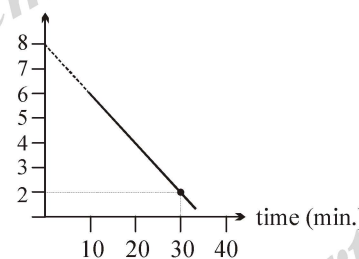
- Q.41 For the first order reaction



following observation is made :

where  $V_t$  (in ml) is volume of  $\text{N}_2$  collected at time  $t$  &  $V_\infty$  (in ml) is volume of  $\text{N}_2$  collected after a long time. What is the time taken (in minute) for 75% reaction ? ( $\log 2 = 0.3$ )

- (A) 2.5 (B) 5.0 (C) 3 (D) 10



- Q.42 The acid catalysed hydrolysis of an organic compound A at 30°C has a time for half change of 100 min., when carried out in a buffer solution at pH = 5, and 10 min., when carried out at pH = 4. Both times of half change are independent of the initial concentration of A. If the rate constant K is given by

$$\frac{-d[A]}{dt} = K[A]^a[H^+]^b, \text{ what are the values of } a \text{ and } b?$$

- (A)  $a = 1, b = 1$  (B)  $a = 2, b = 1$  (C)  $a = 0, b = 1$  (D)  $a = 1, c = 0$

- Q.43 Decomposition of reaction  $3A(g) \longrightarrow 2B(g) + 2C(s)$  follows **first order** kinetics. Starting with **pure A (at 6 atm)**, the pressure developed after 20 minute and after a long time are **5.05 atm** and **4.05 atm**, respectively. Identify the **correct** statement.

- (A) Time for 75% completion is slightly more than 40 minute.  
 (B) Time for 87.5% completion is slightly less than 60 minute.  
 (C) Time for 93.75% completion is exactly 80 minute.  
 (D) Time for 90% completion is more than 80 minute.

- Q.44 The reaction :  $A_{(aq)} \longrightarrow \text{Products}$ , occur 0.01% in 20 milliseconds when the initial concentration of 'A' was 0.4M and 80 milliseconds when the initial concentration of 'A' was 0.2 M. The order of reaction is:

- (A) 0 (B) 1 (C) 2 (D) 3

- Q.45 Under the same reaction conditions, initial concentration of  $1.386 \text{ mol dm}^{-3}$  of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio  $\left(\frac{k_1}{k_0}\right)$  of the rate constants for first order ( $k_1$ ) and zero order ( $k_0$ ) of the reactions is  
 (A)  $0.5 \text{ mol}^{-1} \text{ dm}^3$  (B)  $1.0 \text{ mol dm}^{-3}$  (C)  $1.5 \text{ mol dm}^{-3}$  (D)  $2.0 \text{ mol}^{-1} \text{ dm}^3$

- Q.46 First order reaction is given :  $X \longrightarrow Y$   
 where X and Y both are optically active compounds with specific rotation  $+80^\circ/\text{mole}$  and  $-10^\circ/\text{mole}$  respectively. Initial rotation of pure sample of X was  $20^\circ$  and solution becomes inactive after 22 min then rate constant (in  $\text{min}^{-1}$ ) of given reaction is: [Given :  $\ln 2 = 0.7$  and  $\ln 3 = 1.1$ ]  
 (A) 0.01 (B) 0.05 (C) 0.1 (D) 0.5

- Q.47 For the reaction :  $A_{(\text{aq})} \rightarrow 2B_{(\text{aq})}$ , the concentration of 'B' at different time is given as:

| Time (min) | 0 | 10  | 20  | 30  |
|------------|---|-----|-----|-----|
| [B] (in M) | 0 | 0.2 | 0.4 | 0.6 |

The order of reaction is :

- (A) 0 (B) 0.5 (C) 1.0 (D) 2.0

- Q.48 The following data is obtained for the reaction :  $A_{(\text{aq})} \longrightarrow 2B_{(\text{aq})} + C_{(\text{aq})}$

| Time (min)           | 0   | 20   | 40    | 60     |
|----------------------|-----|------|-------|--------|
| Concentration of 'A' | 0.1 | 0.09 | 0.081 | 0.0729 |

The order of reaction is :

- (A) 0 (B) 1 (C) 2 (D) 3

- Q.49 A first order reaction :  $2P_{(\text{g})} \rightarrow Q_{(\text{g})} + 2S_{(\text{g})}$

| Time (min.)               | 0   | 35  | $\infty$ |
|---------------------------|-----|-----|----------|
| $P_{\text{total}}$ (torr) | 100 | 125 | 150      |

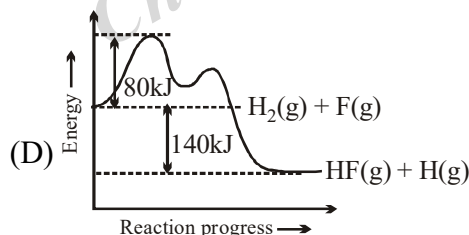
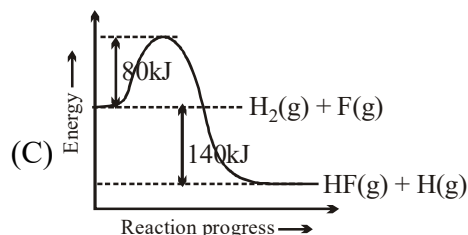
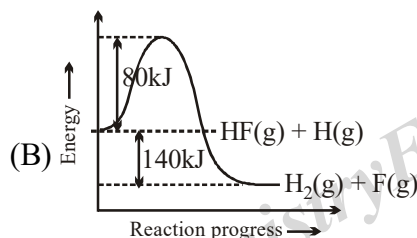
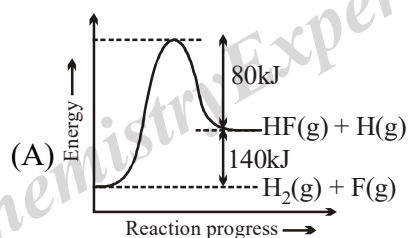
Then rate of reaction will be \_\_\_\_\_ when partial pressure of P is 50 torr.

[Given :  $\ln 2 = 0.7$ ]

- (A) 1 torr/s (B) 0.5 torr/s (C)  $8.33 \times 10^{-3} \text{ torr/s}$  (D) 30 torr/s

- Q.50 For elementary reaction :  $H_2(g) + F(g) \rightarrow HF(g) + H(g)$   $\Delta H = -140 \text{ kJ/mol}$

Activation energy is 80 kJ/mol. Then correct energy diagram is :



Q.51 Rate of a reaction can be expressed by Arrhenius equation as :

$$k = Ae^{-E/RT}$$

In this equation, E represents

- (A) The fraction of molecules with energy greater than the activation energy of the reaction
- (B) The energy above which all the colliding molecules will react
- (C) The energy below which colliding molecules will not react
- (D) The total energy of the reacting molecules at a temperature, T

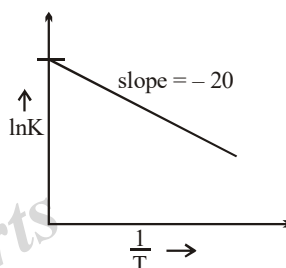
Q.52 The rate constant, the activation energy and the Arrhenius parameter (A) of a chemical reaction at 25°C are  $3.0 \times 10^{-22} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant at  $T \rightarrow \infty$  is

- (A)  $2.0 \times 10^{18} \text{ s}^{-1}$
- (B)  $6.0 \times 10^{14} \text{ s}^{-1}$
- (C) infinity
- (D)  $3.6 \times 10^{30} \text{ s}^{-1}$

Q.53 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

- (A) 43.85 kJ/mol
- (B) 55.14 kJ/mol
- (C) 11.97 kJ/mol
- (D) 6.65 kJ/mol

Q.54 A graph of  $\ln K$  vs  $\frac{1}{T}$  is given :



Where

K is rate constant (in  $\text{s}^{-1}$ )

T is temperature (in K)

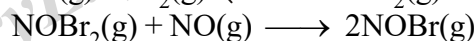
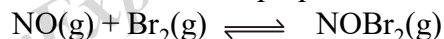
Then fraction of molecules having energy equal to or greater than threshold energy is

- (A)  $e^{20/T}$
- (B)  $e^{20/RT}$
- (C)  $e^{-20/RT}$
- (D)  $e^{-20/T}$

Q.55 The energies of activation for forward and reverse reactions for  $A_2 + B_2 \rightleftharpoons 2AB$  are  $180 \text{ kJ mol}^{-1}$  and  $200 \text{ kJ mol}^{-1}$  respectively. The presence of catalyst lowers the activation energies of both (forward and reverse) reactions by  $100 \text{ kJ mol}^{-1}$ . The magnitude of enthalpy change of the reaction ( $A_2 + B_2 \rightarrow 2AB$ ) in the presence of catalyst will be (in  $\text{kJ mol}^{-1}$ ).

- (A) 300
- (B) 120
- (C) 20
- (D) -20

Q.56 The following mechanism has been proposed for the reaction of NO with  $\text{Br}_2$  to form NOBr :



If the second step is the rate determining step, the order of the reaction with respect to NO(g) is

- (A) 2
- (B) 1
- (C) 0
- (D) 3

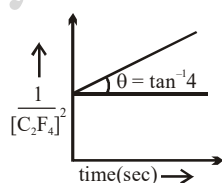
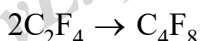
Q.57 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process  $AB + h\nu \rightarrow AB^*$ , the rate of formation of  $AB^*$  is directly proportional to

- (A) C
- (B) I
- (C)  $I^2$
- (D) CI

- Q.58 75 % of a first order reaction occurs in 30 min at 27°C. 87.5 % of the same reaction occurs in 30 min at 57°C. The activation energy of reaction is [ $\ln 2 = 0.7, \ln 3 = 1.1$ ]  
 (A) 2.64 kJ/mol (B) 2.64 Kcal/mol (C) 10.97 Kcal/mol (D) zero

**More than one may be correct**

- Q.59 Select **incorrect** statement(s):  
 (A) Unit of pre-exponential factor (A) for second order reaction is  $\text{mol L}^{-1} \text{s}^{-1}$ .  
 (B) A zero order reaction must be a complex reaction.  
 (C) Molecularity is defined only for RDS in a complex reaction.  
 (D) None of the above statement is incorrect.
- Q.60 Which of the following is/are **correct** statement?  
 (A) Stoichiometry of a reaction tells about the order of the elementary reactions.  
 (B) For a zero order reaction, rate and the rate constant are identical.  
 (C) A zero order reaction is controlled by factors other than concentration of reactants.  
 (D) A zero order reaction is always elementary reaction.
- Q.61 Which of the following statement is **incorrect**?  
 (A) The order of reaction is the sum of powers of all the concentration terms in the rate equation.  
 (B) The order of reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentrations of all other reactants constant.  
 (C) Orders of reactions can not be fractional.  
 (D) The order of a reaction can only be determined from the stoichiometric equation of the reaction.
- Q.62 For the reaction :



Then

- (A) Order of reaction is 3. (B) Half life is  $\frac{3}{4}$  min if initially 1M  $\text{C}_2\text{F}_4$  is taken  
 (C) Reaction must be complex (D) Disappearance constant w.r.t.  $\text{C}_2\text{F}_4$  is  $4 \text{ min}^{-1}$ .
- Q.63 For the gaseous reaction :  $\text{A}_{(g)} \longrightarrow \text{Products}$ , the rate may be expressed as

**Method I :**  $-\frac{1}{V} \cdot \frac{dn_A}{dt} = k_1 \cdot C_A^n$

**Method II :**  $-\frac{dP_A}{dt} = k_2 \cdot P_A^n$

Where  $C_A = \frac{n_A}{V}$  = molar concentration of A and  $P_A$  is the partial pressure of A at time 't' and 'n' is the order of reaction. The reaction is occurring at constant temperature,  $T = 300 \text{ K}$ . Assume ideal behaviour of gas. Select the **correct** statement(s)

- (A)  $k_1 = k_2$  for any value of 'n' (B)  $k_1 = k_2$ , when  $n = 1$   
 (C)  $k_1 = k_2 \cdot (RT)$ , when  $n = 0$  (D)  $k_1 = k_2 \cdot (RT)$ , when  $n = 2$

Assertion & Reasoning type questions

- Q.64 **Statement-1** : A fractional order reaction must be a complex reaction.  
**Statement-2** : Fractional order of RDS equals to overall order of a complex reaction.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- Q.65 **Statement-1** : The time of completion of reactions of type  $A \rightarrow \text{product}$  (order  $< 1$ ) may be determined.  
**Statement-2** : Reactions with order  $\geq 1$  are either too slow or too fast and hence the time of completion can not be determined.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- Q.66 **Statement-1** : The overall rate of a reversible reaction may decrease with the increase in temperature.  
**Statement-2** : When the activation energy of forward reaction is less than that of backward reaction, then the increase in the rate of backward reaction is more than that of forward reaction on increasing the temperature.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- Q.67 **Statement-1** : In a reversible endothermic reaction,  $E_{\text{act}}$  of forward reaction is higher than that of backward reaction  
**Statement-2** : The threshold energy of forward reaction is more than that of backward reaction  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- Q.68 **Statement-1** : A catalyst provides an alternative path to the reaction in which conversion of reactants into products takes place quickly  
**Statement-2** : The catalyst forms an activated complex of lower potential energy, with the reactants by which more number of molecules are able to cross the barrier per unit of time.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

Comprehension

## Paragraph for Question Nos. 69 &amp; 70

For a hypothetical elementary reaction  $A \xrightarrow{k_1} 2B$  where  $\frac{k_1}{k_2} = \frac{1}{2}$   
 $\xrightarrow{k_2} 2C$

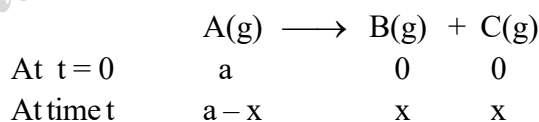
Initially only 2 moles of A are present.

Q.69 The total number of moles of A, B & C at the end of 50% reaction are  
 (A) 2 (B) 3 (C) 4 (D) 5

Q.70 Number of moles of B in the above question  
 (A) 2 (B) 1 (C) 0.666 (D) 0.333

## Paragraph for Question Nos. 71 &amp; 72

A reaction is said to be first order if its rate is proportional to the concentration of reactant. Let us consider a reaction



The rate of reaction is given by the expression  $\frac{dx}{dt} = k(a - x)$  and integrated rate equation for a given reaction is represented as  $k = \frac{1}{t} \ln \left( \frac{a}{a - x} \right)$  where  $a$  = initial concentration and  $(a - x)$  = concentration of A after time  $t$ .

Q.71 Thermal decomposition of compound X is a first order reaction. If 75% of X is decomposed in 100 min. How long will it take for 90% of the compound to decompose?

**Given :  $\log 2 = 0.30$**

(A) 190 min (B) 176.66 min (C) 166.66 min (D) 156.66 min

Q.72 Consider a reaction  $A(g) \longrightarrow 3B(g) + 2C(g)$  with rate constant  $1.386 \times 10^{-2} \text{ min}^{-1}$ . Starting with 2 moles of A in 12.5 litre vessel initially, if reaction is allowed to take place at constant pressure & at 298K then find the concentration of B after 100 min.

(A) 0.04 M (B) 0.36 M (C) 0.09 M (D) None of these



## Paragraph for Question Nos. 73 &amp; 74

For the given sequential reaction



the concentration of A, B & C at any time 't' is given by

$$[A]_t = [A]_0 e^{-k_1 t}$$

$$[B]_t = \frac{k_1 [A]_0}{(k_2 - k_1)} \left[ e^{-k_1 t} - e^{-k_2 t} \right]$$

$$[C]_t = [A]_0 - ([A]_t + [B]_t)$$

Q.73 The time at which concentration of B is maximum is

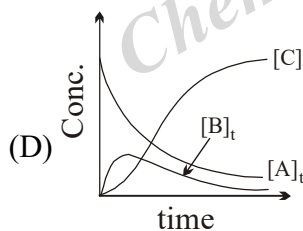
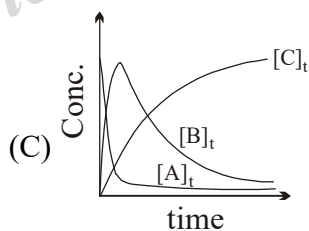
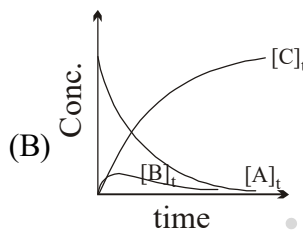
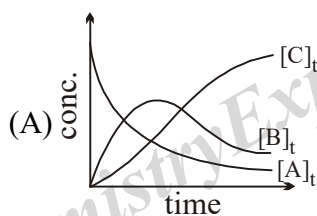
(A)  $\frac{k_1}{k_2 - k_1}$

(B)  $\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$

(C)  $\frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$

(D)  $\frac{k_2}{k_2 - k_1}$

Q.74 Select the correct option if  $k_1 = 1000 \text{ s}^{-1}$  and  $k_2 = 20 \text{ s}^{-1}$ .



Match the column :

Q.75 For the reaction of type  $A(g) \longrightarrow 2B(g)$

**Column-I** contains four entries and **column-II** contains four entries. Entry of column-I are to be matched with ONLY ONE ENTRY of column-II

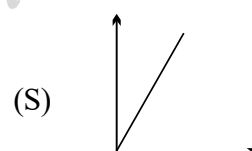
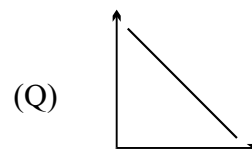
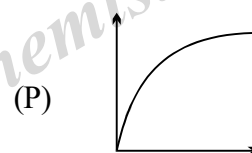
**Column I**

(A)  $\frac{d[B]}{dt}$  vs  $\frac{-d[A]}{dt}$  for first order

(B)  $[A]$  vs  $t$  for first order

(C)  $[B]$  vs  $t$  for first order

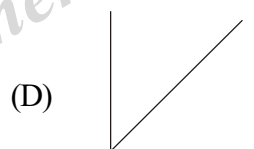
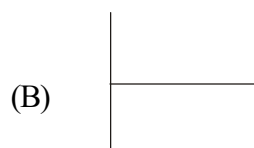
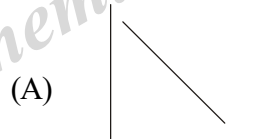
(D)  $[A]$  vs  $t$  for zero order

**Column II**

Q.76 **Column-I** and **column-II**. Entry of column-I are to be matched with ONE OR MORE THAN ONE ENTRIES of column-II and vice versa.

**Column I**

(Graphs reaction  $A \rightarrow \text{Products}$ )

**Column II**

(Co-ordinates)

(P)  $\ln[A]$  (y-axis),  $t$  (x-axis) (order = 1)

(Q)  $t_{1/2}$  (y-axis),  $[A_0]$  (x-axis) (order = 1)

(R)  $r$  (y-axis),  $t$  (x-axis) (order = 0)

(S)  $t_{1/2}$  (y-axis),  $[A_0]$  (x-axis) (order > 1)

(T)  $r$  (y-axis),  $[A]$  (x-axis) (order = 1)

**ANSWER KEY****EXERCISE-1**

- Q.1 (i)  $r = \frac{1}{4} \frac{d[\text{NO}]}{dt} = 9 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ , (ii)  $36 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ , (iii)  $54 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- Q.2  $1.2 \times 10^{-3} \text{ gm/min}$  Q.3 (a)  $2.1 \times 10^{-7} \text{ M/s}$ , (b)  $8.4 \times 10^{-7} \text{ M/s}$ ,  $2.1 \times 10^{-7} \text{ M/s}$
- Q.4  $16 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$  Q.5  $1.5 \text{ torr/s}$  Q.6  $8.12 \times 10^{-6} \text{ Ms}^{-1}$
- Q.7 Rate of formation of  $\text{Cl}^{-1} = 4 \times 10^{-7} \text{ M s}^{-1}$
- Q.8 (a) rate increase by 27 times, (b) rate decreases by 8 times
- Q.9  $1/6$  Q.10 (i)  $7.2 \text{ M}$ , (ii) Think Q.11  $0 \%$
- Q.12  $1.67 \times 10^{-5} \text{ M s}^{-1}$  Q.13  $K = 0.01 \text{ M min}^{-1}$  Q.14  $0.05 \text{ atm/s}$
- Q.15  $0.75 \text{ M}$  Q.16  $6 \times 10^{-9} \text{ sec}$  Q.17  $1.2 \text{ hr}$
- Q.18 (i)  $36 \text{ min.}$ , (ii)  $108 \text{ min.}$  (iii)  $1/8$  Q.19 (i)  $0.0223 \text{ min}^{-1}$ , (ii)  $62.17 \text{ min}$  (iii)  $\approx 0.6$  or  $0.59$
- Q.20  $3.435 \times 10^{-3} \text{ M/min}$  Q.21  $t_{1/2} = 24.14 \text{ min}$
- Q.22  $6.67 \times 10^{-4}$  Q.23  $6 \text{ M}$  Q.24  $3.3 \times 10^{-4} \text{ s}^{-1}$  Q.25  $11.2 \%$
- Q.26  $1.45 \times 10^{-3} \text{ M s}^{-1}$  Q.27  $1.25 \times 10^{-5} \text{ mol s}^{-1}$  Q.28  $6 \times 10^{-6} \text{ s}$
- Q.29 (a)  $0.01 \text{ M}$  (b)  $\frac{20}{3} \text{ min}$  (c)  $\frac{20}{3} \text{ min}$
- Q.30 (a)  $5 \times 10^{-3} \text{ s}^{-1}$  (b)  $0.06 \text{ bar}$  (c)  $1.386 \times 10^2 \text{ s}$
- Q.31 (a) Rate law  $r = K[\text{NH}_4^+]^1 [\text{NH}_2^-]^1$ ; (b)  $3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ; (c)  $6 \times 10^{-5} \text{ Ms}^{-1}$
- Q.32 (a) rate law  $= -\frac{d[\text{A}]}{dt} = k[\text{A}]^1 [\text{B}]^2$ ; (b)  $k = \frac{6 \times 10^{-3}}{10^{-3}} = 6 \text{ M}^{-2} \text{ s}^{-1}$
- Q.33  $1$  Q.34  $3$  Q.35  $0$  Q.36  $3$
- Q.37 First order Q.38  $16 \text{ ml}$  Q.39 (i)  $r = K[(\text{CH}_3)_2\text{O}]$ ,  $0.000428 \text{ s}^{-1}$
- Q.40 (a)  $75 \text{ min}$  (b)  $120 \text{ min}$  Q.41  $k = \frac{1}{t} \ln \frac{P_3}{(P_3 - P_2)}$  Q.42  $k = \frac{1}{t} \ln \frac{r_\infty}{(r_\infty - r_t)}$
- Q.43  $966 \text{ min}$  Q.44 (a)  $90 \text{ mm}$ , (b)  $47 \text{ mm}$ , (c)  $6.49 \times 10^{-2} \text{ min}^{-1}$ , (d)  $10.677 \text{ min.}$
- Q.45  $k_1 = 2.605 \times 10^{-3} \text{ min}^{-1}$  Q.46  $40 \text{ min}$
- Q.47  $0.1 \text{ min}^{-1}$  Q.48  $1.66 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  Q.49  $0.1 \text{ min}^{-1}$
- Q.50  $\frac{1}{e^{(K_1+K_2)t} - 1}$  Q.51  $\frac{[\text{C}]}{[\text{A}]} = \frac{10}{11} (e^{11x} - 1)$  Q.52  $t = 4 \text{ min}$  Q.53  $379.79 \text{ K}$
- Q.54 (a)  $190 \text{ kJ}$ ,  $180 \text{ kJ}$ ; (b)  $\Delta H = 10 \text{ kJ}$ ; (c) Endothermic (As  $\Delta H = +\text{ve}$ ); (d)  $f = e^{-76}$
- Q.55 Fraction  $= e^{-20}$  Q.56  $9.6 \text{ KCal/mol}$  Q.57 (a)  $E_a = 14.4 \text{ KCal}$ , (b)  $528 \text{ M}^{-1} \text{ s}^{-1}$
- Q.58  $54.124 \text{ kJ/mol}$  (a)  $2$ , (b)  $1.5$  Q.59  $1000 \text{ Cal/mol}$
- Q.60 Rate of reaction increases  $e^{100}$  times Q.61  $10.757 \text{ kcal mol}^{-1}$

- Q.62 2.64 Kcal/mol      Q.63 2000 K      Q.64 (a) 660R, (b) 30 hours  
 Q.65 6 Kcal/mol      Q.66 100 kJmol<sup>-1</sup>      Q.67  $E_f = 7200R$ ;  $E_b = 10200R$   
 Q.68  $r = K' [NO]^2 [Br_2]$       Q.69  $r = K [NO]^2 [H_2]$ , where  $K = k_2 \times K_1$

Q.71 (a)  $\frac{d[D]}{dt} = \frac{k_1 k_3 [A][B]}{k_2 + k_3}$ ; (b)  $E_a = E_{a1} + E_{a3} - E_{a2}$ ,  $A = \frac{A_1 A_3}{A_2}$

### EXERCISE-2

- |                                 |         |                                 |          |          |
|---------------------------------|---------|---------------------------------|----------|----------|
| Q.1 B                           | Q.2 C   | Q.3 B                           | Q.4 C    | Q.5 B    |
| Q.6 C                           | Q.7 A   | Q.8 B                           | Q.9 C    | Q.10 B   |
| Q.11 D                          | Q.12 A  | Q.13 D                          | Q.14 D   | Q.15 D   |
| Q.16 B                          | Q.17 A  | Q.18 B                          | Q.19 D   | Q.20 C   |
| Q.21 C                          | Q.22 D  | Q.23 C                          | Q.24 D   | Q.25 C   |
| Q.26 D                          | Q.27 B  | Q.28 C                          | Q.29 B   | Q.30 C   |
| Q.31 B                          | Q.32 C  | Q.33 A                          | Q.34 A   | Q.35 B   |
| Q.36 C                          | Q.37 D  | Q.38 A                          | Q.39 B   | Q.40 A   |
| Q.41 C                          | Q.42 A  | Q.43 C                          | Q.44 D   | Q.45 A   |
| Q.46 C                          | Q.47 A  | Q.48 B                          | Q.49 C   | Q.50 C   |
| Q.51 C                          | Q.52 B  | Q.53 B                          | Q.54 D   | Q.55 C   |
| Q.56 A                          | Q.57 B  | Q.58 B                          | Q.59 ACD | Q.60 ABC |
| Q.61 CD                         | Q.62 AC | Q.63 BD                         | Q.64 C   | Q.65 C   |
| Q.66 A                          | Q.67 C  | Q.68 A                          | Q.69 B   | Q.70 C   |
| Q.71 C                          | Q.72 C  | Q.73 C                          | Q.74 C   |          |
| Q.75 (A) S, (B) R, (C) P, (D) Q |         | Q.76 (A) P (B) Q, R (C) S (D) T |          |          |

**EXERCISE-1 (Subjective Questions)****CALCULATION OF MOLE**

- Q.1 Calculate the following quantities :
- Mass, in grams, of 0.1 mol of sucrose ( $C_{12}H_{22}O_{11}$ )
  - Moles of  $Zn(NO_3)_2$  in 142.05 g of this substance
  - Number of molecules of  $HCOOH$  in  $10^{-6}$  mol.
  - Number of N-atom in 0.2 mol of  $N_2H_4$ .
  - Number of O-atom in  $2 \times 10^{-3}$  mol  $Al(NO_3)_3$ .
  - Number of moles of  $NH_4Cl$  in 107 g of this substance.
  - Mass, in grams of  $2 \times 10^{-3}$  mol of  $CdS$
  - Molar mass of Cholesterol if 0.00105 mol has a mass of 0.525 g
  - Mass, in grams, of  $3 \times 10^{21}$  molecules of Aspirin,  $C_9H_8O_4$
  - Molar mass of an element if mass of 1 atom is  $12 \times 10^{-24}$  g.
  - Number of  $SO_4^{2-}$  ions in 19.6 g  $Cr_2(SO_4)_3$
  - Number of  $Ca^{2+}$  ions in 6.2 g  $Ca_3(PO_4)_2$
- Q.2 Nitric acid is composed of  $HNO_3$  molecules. If a sample weighing 6.3 g  $HNO_3$  then calculate
- How many nitrogen atoms are in this sample?
  - How many oxygen atoms are in 2.52 gm of nitric acid.
- Q.3 Ethanol,  $C_2H_5OH$ , is the substance commonly called alcohol. The density of liquid alcohol is 0.7893 g/ml at 293 K. If 1.2 mole of ethanol are needed for a particular experiment, what volume of ethanol should be measured out?
- Q.4 A gaseous mixture contains  $CO_2$  (g) and  $N_2O$  (g) in a 2 : 5 ratio by mass. Find the ratio of the number of molecules of  $CO_2$  (g) and  $N_2O$  (g)
- Q.5 Find the number of neutrons in 0.45 g water, assuming that all the hydrogen atoms are  $H^1$  atoms and all the oxygen atoms are  $O^{16}$  atoms
- Q.6 A 12.6 g sample of  $Na_2SO_3$  is mixed with 30 g sample of  $MgSO_4$ . What is total mass of oxygen present in the mixture?
- Q.7 Calcium carbonate is a common ingredient in stomach antacids. If one antacid tablet has 60 mg of  $CaCO_3$ , how many moles of  $CaCO_3$  are there in 200 tablets.
- Q..8 A 3L sample of paint that has a density of 5 g/ml is found to contain 10% by mass  $Pb_3N_2$ (s). How many grams of lead were in the paint sample? [Atomic mass of Pb = 207]
- Q.9 Calculate the following quantities :
- Number of moles of 11.2 L  $CO_2$  at NTP
  - Number of moles of 2L  $CO_2$  at 16.42 atm pressure and  $127^\circ C$ .
  - Molar mass of gas at 1atm and  $27^\circ C$  having density  $1.2 \times 10^{-3}$  g/ml
  - Number of moles of 45.4 L  $O_2$  at STP

Q.10 Complete the following table for an ideal gas

|       | P                               | V     | n                  | Temperature |
|-------|---------------------------------|-------|--------------------|-------------|
| (i)   | $16.628 \times 10^3 \text{ Pa}$ | 15 L  | _____              | 27°C        |
| (ii)  | _____                           | 42 L  | 0.42 mol           | 200K        |
| (iii) | 304 torr                        | _____ | $4 \times 10^{-2}$ | 327°C       |
| (iv)  | 380 mmHg                        | _____ | 0.5 mol            | 300K        |

Q.11 What is the density of  $\text{CCl}_4(\text{g})$  (in g/L) at 380 torr and 127°C ?

Q.12 Calculate the total pressure (in atm) of a mixture of 0.02 mol of  $\text{He}(\text{g})$  and 0.01 mol of  $\text{H}_2(\text{g})$  in 3 L flask at 127°C.

Q.13 Calculate the following quantities :

- Molar mass of oxygen gas if 64 g of oxygen in 22.4 L vessel exerts a pressure of 2 atm at 0°C.
- Average molar mass of 20 gm mixture of  $\text{CH}_4(\text{g})$  and  $\text{He}(\text{g})$  in 11.2 L vessel exerts a pressure of 5 atm at 0°C.
- Calculate atomicity of phosphorus if 62g of phosphorus exerts a pressure of 0.5 atm in 22.4 L vessel at 0°C.
- Calculate molar mass of gas having density  $2 \times 10^{-3} \text{ g/cm}^3$  at 1 atm and 0°C.

#### AVERAGE ATOMIC MASS & AVERAGE MOLAR MASS

Q.14 The vapour density of a gaseous mixture of non-reactive gases 'A' and 'B' is 40. If the molar mass of gas 'A' is 20 gm/mol and the mixture contains the gases in 2 : 3 volume ratio, then Calculate molar mass of gas 'B' :

Q.15 2 isotopes of an element are present in 1 : 2 ratio of number, having mass number M and (M + 0.5) respectively. Find the mean mass number of element.

Q.16 A hypothetical element Z is found to have an atomic mass of 37.45 amu. Element Z has only two isotopes,  $\text{Z}^{37}$  and  $\text{Z}^{38}$ . The  $\text{Z}^{37}$  isotope has a fractional abundance of 0.77 and isotopic mass of 37.24. What is the isotopic mass of the other isotope.

Q.17 Silver has two naturally occurring isotopes, one of mass 107 amu and other of mass 109 amu. Find fraction of abundances for these two isotopes. The atomic mass is 107.8 amu.

Q.18 The relative density of a mixture of  $\text{CO}_2(\text{g})$  &  $\text{H}_2\text{O}(\text{g})$  w.r.t. gaseous hydrogen atoms is 30. Then Calculate mol percentage of  $\text{CO}_2$

#### EMPIRICAL FORMULA & MOLECULAR FORMULA

Q.19 Give the empirical formula of each of the following compound if a sample contains.

- 0.013 mol C, 0.039 mol H and 0.0065 mol oxygen(O)
- 11.66 g Fe and 5.01 g oxygen(O)
- 40% C, 6.7% H and 53.3% oxygen (O) by mass.

Q.20 What is the molecular formula of each of following compounds?

- Empirical formula  $\text{CH}_2$ , molar mass = 84 gm/mol
- Empirical formula  $\text{NH}_2\text{Cl}$ , molar mass = 51.5 gm/mol

- Q.21 During an analysis of 180 mg of a molecule that contains only C, H and O. As a result 264 mg  $\text{CO}_2$  is produced along with 108 mg  $\text{H}_2\text{O}$   
 (a) If the molecule contains only C, H and O, what is empirical formula?  
 (b) If the molar mass of the compound is 60 g/mol, what is molecular formula of the compound?
- Q.22 0.078 gms of a gaseous hydrocarbon occupy 44.8 ml volume at 1 atm and  $273^\circ\text{C}$ . The empirical formula of the hydrocarbon is CH. Find total number of atoms in one molecule of the hydrocarbon.
- Q.23 The empirical formula of styrene is  $\text{CH}$ ; the molar mass of styrene is 104 g/mol. What number of H atoms are present in a 2.08g sample of styrene
- Q.24 A compound whose empirical formula is  $\text{XF}_3$  consists of 65% F by mass. What is the atomic mass of X?

### CONCENTRATION TERMS

- Q.25 Calculate the molarity of the following solutions :  
 (a) 4g of caustic soda is dissolved in 200 mL of the solution.  
 (b) 5.3 g of anhydrous sodium carbonate is dissolved in 100 mL of solution.  
 (c) 0.365 g of pure HCl gas is dissolved in 50 mL of solution.
- Q.26 Density of a solution containing 14% by mass of sulphuric acid is 1.05 gm/mL. What is the molarity of solution ?
- Q.27 15 g of methyl alcohol is present in 100 mL of solution. If density of solution is  $0.90 \text{ gm mL}^{-1}$ . Calculate the mass percentage of methyl alcohol in solution
- Q.28 A 6.90 M solution of KOH in water contains 30% by mass of KOH. What is density of solution?
- Q.29 Aqueous solution of urea has density 1.5 g/ml and it is 5 M. Calculate  
 (a) Its molality (b) w/w %  
 (c) w/v % (d) mole fraction of solute
- Q.30 A bottle of whisky contains 12% aqueous ethanol by volume. The density of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is  $0.8 \text{ g/cm}^3$ . Calculate.  
 (a) molality (b) molarity (c) w/w%
- Q.31 Calculate the number of moles of solute present in each of the following aqueous solutions.  
 (a) 600 ml of 0.25 M  $\text{CaCl}_2$   
 (b) 100 g of 0.2 M KCl, density of solution = 1.2 gm/ml  
 (c) 120 g of a solution that is 9% glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) by mass  
 (d) 200 ml of solution, that is 2M in urea ( $\text{NH}_2\text{CONH}_2$ ). [Given : density of solution 1.2 g/ml]  
 (e) 100 ml of 5M NaCl
- Q.32 Units of parts per million (ppm) or per billion (ppb) are often used to describe the concentrations of solutes in very dilute solutions. The units are defined as the number of grams of solute per million or per billion grams of solvent. Bay of Bengal has 1.89 ppm of lithium ions. What is the molality of  $\text{Li}^+$  in this water ? ( $\text{Li} = 7$ )
- Q.33 The average concentration of  $\text{Na}^+$  ion in human body is 3 to 4 gm per litre. What is the approximate molarity of  $\text{Na}^+$  ion in body?

- Q.34 What is the concentration of chloride ion, in molarity, in a solution containing 10.56 gm  $\text{BaCl}_2 \cdot 8\text{H}_2\text{O}$  per litre of solution ? (Ba = 137)
- Q.35 An aqueous solution which is 20% (w/w) and 30% (w/v) in NaOH. What will be mass fraction of water in 30 ml of such solution.
- Q.36 The concentration of a solution is 8% (w/w) and 10% (w/v). Calculate density of solution?
- Q.37 The mole fraction of solute in aqueous urea solution is 0.2. Calculate the mass percent of solute ?
- Q.38 The concentration of  $\text{Ca}(\text{HCO}_3)_2$  in a sample of hard water is 486 ppm. The density of water sample is 1.0 gm/ml. Calculate the molarity of solution ?
- Q.39 Calculate molality (m) of each ion present in the aqueous solution of 2M  $\text{NH}_4\text{Cl}$  assuming 100% dissociation according to reaction.
- $$\text{NH}_4\text{Cl (aq)} \longrightarrow \text{NH}_4^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$
- Given :** Density of solution = 3.107 gm / ml.

Q.40 Fill in the blank :

| <i>Aqueous solution</i> | <i>Density(g/ml)</i> | <i>Mass% of solute</i> | <i>m</i> | <i>M</i> | <i>Mole fraction of solute(X)</i> |
|-------------------------|----------------------|------------------------|----------|----------|-----------------------------------|
| Urea                    | 1.2                  | 20                     | _____    | _____    | _____                             |
| Acetic acid             | 1.2                  | 40                     | _____    | _____    | _____                             |
| HCl                     | 1.5                  | 30                     | _____    | _____    | _____                             |
| Ammonia                 | 1.25                 | 20                     | _____    | _____    | _____                             |

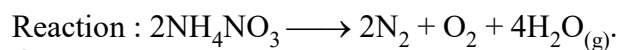
## PROBLEMS RELATED WITH MIXING & DILUTION

- Q.41 300gm of an aqueous solution of a particular solute (containing 30% by mass solute) is mixed with 400 gm of another aq. solution of same solute (containing 40% solute by mass). In the final solution calculate. [Given : density of final solution =  $7/8$  gm/ml, Molecular mass of solute = 50]
- (i) Mass % of solute (ii) Mole fraction of solute  
(iii) Molarity (iv) Molality
- Q.42 10L of 2M NaCl solution is subjected to following changes. Calculate final molarity in each case. If solution is :
- (i) Diluted by 20L (ii) Diluted to 20L  
(iii) Heated until the volume reduced to 40%  
(iv) Heated until the volume reduced by 40%  
(v) 2 mole of NaCl(s) is further dissolved. (Neglect change in volume)
- Q.43 (a) 500 ml 1M  $\text{H}_2\text{SO}_4$  solution is mixed with 400 ml of 2.5 M HCl solution. Density of final solution is 1.2 gm/ml. Calculate  $[\text{H}^+]$  in the final solution.  
(b) 500 ml 1M  $\text{H}_2\text{SO}_4$  solution ( $d_{\text{solution}} = 1.4$  g/ml) is mixed with 400 ml of 2.5 M HCl solution ( $d_{\text{solution}} = 1.25$  g/ml) to give a final solution of density 1.2 g/ml. Calculate  $[\text{H}^+]$  in final solution.

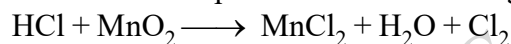


**STOICHIOMETRY AND LIMITING REAGENT**

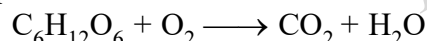
- Q.44 What total volume, in litre at 627°C and 1 atm, could be formed by the decomposition of 16 gm of  $\text{NH}_4\text{NO}_3$  ?



- Q.45 How many gm of HCl is needed for complete reaction with 69.6 gm  $\text{MnO}_2$  ?

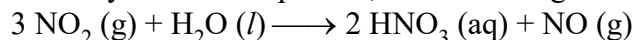


- Q.46 Carbon dioxide is end product of metabolism as shown :



Calculate daily production of  $\text{CO}_2$  (**in grams**) assuming each person consumes  $5 \times 10^2$  gm glucose perday and world's population is 3.6 billion.

- Q.47 Nitric acid is manufactured by the Ostwald process, in which nitrogen dioxide reacts with water.



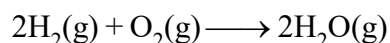
How many grams of nitrogen dioxide are required in this reaction to produce 25.2 gm  $\text{HNO}_3$  ?

- Q.48 Urea,  $\text{NH}_2\text{CONH}_2$ , is a nitrogen fertilizer that is manufactured from ammonia and  $\text{CO}_2(\text{g})$



What volume of ammonia at 27°C and 8.21 atm is needed to produce 900 g urea?

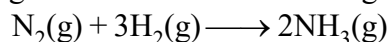
- Q.49 Consider the reaction :



Identify the limiting reagent in each of the reaction mixtures given below and calculate  $\text{H}_2\text{O}(\text{g})$ .

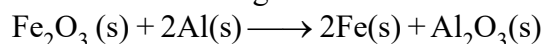
- (a) 50 molecules of  $\text{H}_2$  and 25 molecules of  $\text{O}_2$
- (b) 100 molecules of  $\text{H}_2$  and 40 molecules of  $\text{O}_2$
- (c) 100 molecules of  $\text{H}_2$  and 100 molecules of  $\text{O}_2$
- (d) 0.5 mol of  $\text{H}_2$  and 0.75 mol of  $\text{O}_2$
- (e) 0.8 mol of  $\text{H}_2$  and 0.75 mol of  $\text{O}_2$
- (f) 4 g of  $\text{H}_2$  and 8 g  $\text{O}_2$
- (g) 5 g of  $\text{H}_2$  and 64 g  $\text{O}_2$

- Q.50 Nitrogen and hydrogen gases react to form ammonia gas as follows :



- (a) At certain temperature and pressure 1.2 L of  $\text{N}_2$  reacts with 3.6 L of  $\text{H}_2$  then, what will be the volume of  $\text{NH}_3$  produced.
- (b) At certain temperature if  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  are taken in a closed rigid vessel at 2atm and 8 atm respectively then what would be the final pressure after the reaction .
- (c) At certain temperature if  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  are taken taken in a closed rigid vessel at 2atm and 8 atm respectively and 20 % reaction takes place then what would be the final pressure after the reaction .

- Q.51 Following reaction is used in thermite welding :



Calculate moles of each reaction compound after the reaction if initially following mixture is taken.

- (a) 2 mol  $\text{Fe}_2\text{O}_3$  + 2 mol  $\text{Al}(\text{s})$
- (b) 5 mol  $\text{Fe}_2\text{O}_3$  + 4 mol  $\text{Al}(\text{s})$
- (c) 10 mol  $\text{Fe}_2\text{O}_3$  + 10 mol  $\text{Al}(\text{s})$
- (d) 0.25 mol  $\text{Fe}_2\text{O}_3$  + 1 mol  $\text{Al}(\text{s})$

- Q.52 Potassium nitrate ( $\text{KNO}_3$ ) is used as a fertilizer for certain crops. It is produced through the reaction :  

$$4\text{KCl} + 4\text{HNO}_3 + \text{O}_2 \longrightarrow 4\text{KNO}_3 + 2\text{Cl}_2 + 2\text{H}_2\text{O}$$
 Calculate the minimum mass of KCl required to produce 505 g  $\text{KNO}_3$ . What mass of  $\text{Cl}_2$  will be generated as well?
- Q.53 Hydrogen cyanide is produced industrially from the reaction of gaseous ammonia, oxygen and methane.  

$$2\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) + 2\text{CH}_4(\text{g}) \longrightarrow 2\text{HCN}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
 If 6.8 kg each of  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{CH}_4$  are reacted then calculate mass of  $\text{HCN}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  formed.
- Q.54 Carbon reacts with chlorine to form  $\text{CCl}_4$ . 36 gm of carbon was mixed with 142 gm of  $\text{Cl}_2$ . Calculate mass of  $\text{CCl}_4$  produced and the remaining mass of reactant.

**PERCENTAGE YIELD AND PERCENTAGE PURITY**

- Q.55 Titanium dioxide,  $\text{TiO}_2$ , reacts with carbon and chlorine to give gaseous  $\text{TiCl}_4$  :  

$$\text{TiO}_2 + 2\text{C} + 2\text{Cl}_2 \longrightarrow \text{TiCl}_4 + 2\text{CO}$$
 The reaction of 7.98 Kg  $\text{TiO}_2$  with excess C and  $\text{Cl}_2$  gives 4.745 Kg  $\text{TiCl}_4$ .  
**[Given : Atomic mass Ti = 47.8]**  
 (a) Calculate amount of  $\text{CO}(\text{g})$  formed (in g)  
 (b) Calculate percentage yield of reaction.
- Q.56 Consider the reaction :  

$$\text{P}_4(\text{s}) + \text{F}_2(\text{g}) \longrightarrow \text{PF}_3(\text{g})$$
 What mass of  $\text{F}_2$  is needed to produce 176 g of  $\text{PF}_3$  if the reaction has 80% yield.
- Q.57 Ammonia gas can be prepared by reaction of a metal oxide such as calcium oxide with  $\text{NH}_4\text{Cl}$ .  

$$\text{CaO}(\text{s}) + \text{NH}_4\text{Cl}(\text{s}) \longrightarrow 2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{CaCl}_2(\text{s})$$
 (a) If 112 g of CaO and 224 g  $\text{NH}_4\text{Cl}$  are mixed, what mass of  $\text{NH}_3$  can be prepared?  
 (b) In above case if 17 g of  $\text{NH}_3$  is obtained, then what is its percentage yield?
- Q.58 A power company burns approximately 475 tons of coal per day to produce electricity. If the sulphur content of the coal is 1.2 % by weight, how many tons  $\text{SO}_2$  are dumped into the atmosphere each day?
- Q.59 Calculate the percent loss in weight after complete decomposition of a pure sample of potassium chlorate.  

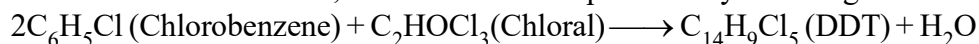
$$\text{KClO}_3(\text{s}) \longrightarrow \text{KCl}(\text{s}) + \text{O}_2(\text{g})$$
- Q.60 In reaction :  

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{HF}$$
 6 Kg of  $\text{CaF}_2$  are treated with an excess of  $\text{H}_2\text{SO}_4$  and yield 2.0 kg of HF. Calculate the percentage yield of reaction :
- Q.61 Cyclohexanol is dehydrated to cyclohexene on heating with conc.  $\text{H}_2\text{SO}_4$ . If the yield of this reaction is 75%, how much cyclohexene will be obtained from 100 gm of cyclohexanol ?  

$$\text{C}_6\text{H}_{12}\text{O} \xrightarrow{\text{con. H}_2\text{SO}_4} \text{C}_6\text{H}_{10}$$
- Q.62 When heated, lithium reacts with nitrogen to form lithium nitride :  

$$\text{Li}(\text{s}) + \text{N}_2(\text{g}) \longrightarrow \text{Li}_3\text{N}(\text{s})$$
 When 21 gm of Li reacts with 280 gm of  $\text{N}_2$  then 0.35 gm of  $\text{Li}_3\text{N}$  is formed. What is percentage yield of the reaction.

Q.63 DDT, an insecticide harmful to fish, birds and humans is produced by following reactions :



If 1125 g of  $\text{C}_6\text{H}_5\text{Cl}$  is reacted with 442.5 g of Chloral.

- What mass of DDT is formed?
- Which reactant is limiting? Which is in excess?
- What mass of excess reactant is left over.
- If 354.5g DDT is formed, then what is the percentage yield?

### **PROBLEMS RELATED WITH MIXTURE**

- Q.64 39 gm of an alloy of aluminium and magnesium when heated with excess of dil. HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen collected at  $0^\circ\text{C}$  has a volume of 44.8 litres at 1 atm pressure. Calculate the composition of the aluminium by moles.
- Q.65 A sample containing only  $\text{CaCO}_3$  and  $\text{MgCO}_3$  is ignited to CaO and MgO. The mixture of oxides produced weight exactly half as much as the original sample. Calculate the mass percentages of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in the sample.
- Q.66 Determine the percentage composition of a mixture (by mass) of anhydrous sodium carbonate and sodium bicarbonate from the following data:  
 Weight of the mixture taken = 2 gm  
 Loss in weight on heating = 0.124 gm.

### **PRINCIPLE OF ATOM CONSERVATION(POAC)**

- Q.67 An 13.8 g sample of  $\text{K}_2\text{CO}_3$  was treated in such a way that all of its carbon was captured in compound  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ . Compute mass of this product in grams.
- Q.68 A chemist dissolves 1.95 g pure platinum (Pt) in an excess of a mixture of hydrochloric acid and nitric acids and then after a series of subsequent steps involving several other chemicals, isolates a compound of molecular formula  $\text{Pt}_2\text{C}_{10}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_6$ . Determine mass of this product in grams.
- Q.69 A sample of mixture of  $\text{CaCl}_2$  and NaCl weighing 5.55 gm was treated to precipitate all the Ca as  $\text{CaCO}_3$  which was then heated and quantitatively converted to 1.68 gm of CaO. Calculate the mass percentage of  $\text{CaCl}_2$  in the mixture.
- Q.70 When 4 gm of a mixture of  $\text{NaHCO}_3$  and NaCl is heated, 0.66 gm  $\text{CO}_2$  gas is evolved. Determine the percentage composition of the original mixture by mass.
- Q.71 Disilane( $\text{Si}_2\text{H}_6$ ) is a gas that reacts with oxygen to give silica( $\text{SiO}_2$ ) and water. Calculate mass of silica that would form if  $100\text{ cm}^3$  Disilane (with a density  $2.48 \times 10^{-3}\text{ gm cm}^{-3}$ ) reacted with excess oxygen.
- Q.72 For  $\text{BaCl}_2 \cdot x\text{H}_2\text{O}$ , if 2.1 gm of compound gives 2 gm of anhydrous  $\text{BaSO}_4$  upon treatment with  $\text{H}_2\text{SO}_4$ . Then calculate value of 'x'.
- Q.73 6 gm of silver salt of tribasic acid gives 4.32 gm silver on strong heating. Calculate the molar mass of the acid.
- Q.74 On complete combustion, 0.1 g of an organic compound gave 0.176g of carbon dioxide and 0.18 g of water. Determine the percentage composition of carbon and hydrogen in the compound.

- Q.75 In Duma's method for estimation of nitrogen, 0.3g of an organic compound gave 24.63 mL of nitrogen collected over water at 300K temperature and 775 mm of Hg pressure. Calculate the percentage composition of nitrogen in the compound. (Vapour pressure of water at 300K=15 mm of Hg)
- Q.76 During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound requires 10 mL of 1 M  $\text{H}_2\text{SO}_4$  for complete neutralisation. Find out the percentage of nitrogen in the compound.
- Q.77 In Carius method of estimation of halogen, 1 g of an organic compound gave 0.094 g of AgBr. Find out the percentage of bromine in the compound.
- Q.78 In sulphur estimation, 0.64 g of an organic compound gave 0.466 g of barium sulphate. What is the percentage of sulphur in the compound?
- Q.79 Equal weights of mercury and iodine are allowed to react completely to form a mixture of mercurous and mercuric iodide leaving none of the reactants. Calculate the ratio by weight of  $\text{HgI}_2$  and  $\text{Hg}_2\text{I}_2$  formed (Hg = 200, I = 127)
- Q.80 Sulphur trioxide may be prepared by the following two reactions :
- $$\text{S}_8 + 8\text{O}_2(\text{g}) \longrightarrow 8\text{SO}_2(\text{g})$$
- $$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$$
- How many grams of  $\text{SO}_3$  will be produced from 1 mol of  $\text{S}_8$ ?
- Q.81
- $$2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$$
- $$3\text{SO}_2 + 2\text{HNO}_3 + 2\text{H}_2\text{O} \longrightarrow 3\text{H}_2\text{SO}_4 + 2\text{NO}$$
- According to the above sequence of reactions, how much  $\text{H}_2\text{SO}_4$  will 1200 gm of PbS produce? (Pb = 208)

### VOLUME STRENGTH

- Q.82 500 ml of a  $\text{H}_2\text{O}_2$  solution on complete decomposition produces 2 moles of  $\text{H}_2\text{O}$ . Calculate the volume strength of  $\text{H}_2\text{O}_2$  solution? [Given : Volume of  $\text{O}_2$  is measured at 1atm and 273 K]
- Q.83 Calculate the %(w/w) strength of 5.6 volume  $\text{H}_2\text{O}_2$  solution of density 1 gm/ml.

### EUDIOMETRY

- Q.84 10 ml of a mixture of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{N}_2$  exploded with excess of oxygen gave a contraction of 6.5 ml. There was a further contraction of 7 ml, when the residual gas treated with KOH. Volume of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{N}_2$  respectively is
- Q.85 When 100 ml of a  $\text{O}_2 - \text{O}_3$  mixture was passed through turpentine, there was reduction of volume by 20 ml. If 100 ml of such a mixture is heated, what will be the increase in volume?
- Q.86 60 ml of a mixture of nitrous oxide and nitric oxide was exploded with excess of hydrogen. If 38 ml of  $\text{N}_2$  was formed, calculate the volume of each gas in the mixture.
- Q.87 When a certain quantity of oxygen was ozonised in a suitable apparatus, the volume decreased by 4 ml. On addition of turpentine the volume further decreased by 8 ml. All volumes were measured at the same temperature and pressure. From these data, establish the formula of ozone.

- Q.88 10 ml of ammonia were enclosed in an eudiometer and subjected to electric sparks. The sparks were continued till there was no further increase in volume. The volume after sparking measured 20 ml. Now 30 ml of  $O_2$  were added and sparking was continued again. The new volume then measured 27.5 ml. All volumes were measured under identical conditions of temperature and pressure. Calculate the molecular formula of ammonia. Nitrogen and Hydrogen are diatomic.
- Q.89 20 ml of a mixture of  $C_2H_2$  and CO was exploded with 30 ml of oxygen. The gases after the reaction had a volume of 34 ml. On treatment with KOH, 8 ml of oxygen remained. Calculate the composition of the mixture.
- Q.90 10 ml of CO is mixed with 25 ml air having 20%  $O_2$  by volume. What would be the final volume if none of CO and  $O_2$  is left after the reaction?
- 
-

**EXERCISE-2 (Objective Questions)****Single Correct:**

- Q.1 The percentage by mole of  $\text{NO}_2$  in a mixture of  $\text{NO}_2(\text{g})$  and  $\text{NO}(\text{g})$  having average molecular mass 34 is :  
 (A) 25% (B) 20% (C) 40% (D) 75%
- Q.2 For the following reaction if equal mass of A and B are taken :  

$$\text{A} + 2\text{B} \rightarrow \text{C}$$
 Which of the following is **correct**? ( $M_A$  and  $M_B$  are molar masses of A and B respectively)  
 (A) If  $M_A = 2M_B$ , then none of the reactant will be left.  
 (B) If  $M_B > \frac{M_A}{2}$ , then A will be limiting reagent.  
 (C) If  $M_A = M_B$ , then A will be limiting reagent  
 (D) All are correct
- Q.3 74 gm of a compound on complete combustion gives 132 gm  $\text{CO}_2$  and 54 gm of  $\text{H}_2\text{O}$ . The molecular formula of the compound may be  
 (A)  $\text{C}_5\text{H}_{12}$  (B)  $\text{C}_4\text{H}_{10}\text{O}$  (C)  $\text{C}_3\text{H}_6\text{O}_2$  (D)  $\text{C}_3\text{H}_7\text{O}_2$
- Q.4 The mass of  $\text{CO}_2$  produced from 620 gm mixture of  $\text{C}_2\text{H}_4\text{O}_2$  &  $\text{O}_2$ , prepared to produce maximum energy is (Combustion reaction is exothermic)  
 (A) 413.33 gm (B) 593.04 gm (C) 440 gm (D) 320 gm
- Q.5 Maximum mass of sucrose  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  produced by mixing 84 gm of carbon, 12 gm of hydrogen and 56 lit.  $\text{O}_2$  at 1 atm & 273 K according to given reaction, is  

$$\text{C}(\text{s}) + \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$$
 (A) 138.5 (B) 155.5 (C) 172.5 (D) 199.5
- Q.6 Cupric nitrate is prepared by dissolving a weighed amount of copper metal in a nitric acid solution,  

$$\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$$
 What mass of  $\text{Cu}(\text{NO}_3)_2$  formed by using 50 mL of 6.0 M  $\text{HNO}_3$ .  
 (A) 112.5 g (B) 21.1 g (C) 168.7 g (D) 42.2 g
- Q.7 If mass of 2 atoms is  $4 \times 10^{-23}$  gm. Then atomic mass of element will be : [Take :  $N_A = 6 \times 10^{23}$  / mole]  
 (A) 24 (B) 12 (C) 6 (D) 2
- Q.8 If 200 ml of 0.1 M  $\text{Na}_2\text{SO}_4$  is mixed with 100 ml of 0.2 M  $\text{Na}_3\text{PO}_4$  solution. Molarity of  $\text{Na}^+$  in the final solution, if final solution has density 1.2 gm/ml.  
 (A) 0.196 M (B) 0.33 M (C) 0.5 M (D) None of these
- Q.9 The number of carbon atoms present in a signature, if a signature written by carbon pencil weights  $1.2 \times 10^{-3}$  gm is  
 (A)  $12.04 \times 10^{20}$  (B)  $6.02 \times 10^{19}$  (C)  $3.01 \times 10^{19}$  (D)  $6.02 \times 10^{20}$
- Q.10 The average atomic mass of a mixture containing 79 mole % of  $^{24}\text{Mg}$  and remaining 21 mole % of  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ , is 24.31. % mole of  $^{26}\text{Mg}$  is  
 (A) 5 (B) 20 (C) 10 (D) 15



- Q.11 An organic compound contains 14 atoms of carbon per molecule. If mass % of carbon in the compound is 22.4 % then molecular mass of the compound will be  
(A) 3000 (B) 750 (C) 12000 (D) 600
- Q.12 An organic compound contains 8 % Oxygen and 4 % Sulphur by mass. Find the minimum possible molecular weight of compound?  
(A) 400 (B) 200 (C) 800 (D) 1600
- Q.13 When 280 gm of ethylene polymerises to polyethylene according to the equation:  

$$n(\text{CH}_2 = \text{CH}_2) \longrightarrow -(\text{CH}_2 - \text{CH}_2)_n$$
 The weight and mole of polyethylene formed will be  
 (A) 280, 10 n (B)  $\frac{280}{n}$ , n (C)  $\frac{28}{n}$ , 280 (D) 280,  $\frac{10}{n}$
- Q.14 6.0 gm of silver salt of a tetrabasic acid gives 4.32 gm silver on strong heating. The molar mass of the acid is (Ag = 108)  
(A) 168 (B) 172 (C) 84 (D) 88
- Q.15 The number of moles of compound  $(\text{KHC}_2\text{O}_4)_{0.95} \cdot \text{H}_2\text{C}_2\text{O}_4$  in its pure sample if sample contains 4 moles of oxygen atoms.  
(A) 0.5 (B)  $0.5 \times 0.95$  (C)  $\frac{4}{(4+0.95 \times 4)}$  (D)  $\frac{4}{0.95}$
- Q.16 20 gm of a mixture of NaCl and NaOH exactly requires 7.3 gm HCl for complete reaction. The mass percent of NaCl in the original mixture is :  
(A) 40% (B) 60% (C) 50% (D) 80%
- Q.17 For a solution concentration can be expressed as 16% w/w as well as 20% w/v. What will be density of solution?  
(A) 1.25 gm/lit. (B) 0.8 gm/lit. (C) 1.25 gm/ml (D) 0.8 gm/ml
- Q.18 In Delhi on a polluted day, concentration of  $\text{SO}_2$  in air is 40 ppm. Assuming density of air is 2gm/litre. How many gram of  $\text{SO}_2$  is present in 100 litre of air?  
(A) 4 mg (B) 4 gm (C)  $8 \times 10^{-3}$  kg (D) 8 mg
- Q.19 The legal limit for human exposure to CO in the work place is 35 ppm. Assuming that the density of air is 1.3 g/L, how many grams of CO are in 1.0L of air at the maximum allowable concentration?  
(A)  $4.55 \times 10^{-5}$  gm (B)  $3.5 \times 10^{-5}$  gm (C)  $2.69 \times 10^{-5}$  gm (D)  $7.2 \times 10^{-5}$  gm
- Q.20 Molarity of pure water if its density is 0.90 gm/ml at 90°C,  
(A) 55.55 M (B) 5.55 M (C) 50 M (D) None of these
- Q.21 If 2M, 200 ml HCl, 2M, 100 ml  $\text{CaCl}_2$  and 5M, 200 ml  $\text{AlCl}_3$  is mixed then final concentration of  $\text{Cl}^-$  will be:  
(A) 2.5 M (B) 3 M (C) 3.5 M (D) 7.6 M

- Q.22 What volumes should you mix of 0.2 M NaCl and 0.1 M  $\text{CaCl}_2$  solution so that in resulting solution the concentration of positive ion is 40% lesser than concentration of negative ion. Assuming total volume of solution 1000 ml.  
 (A) 400 ml NaCl, 600 ml  $\text{CaCl}_2$  (B) 600 ml NaCl, 400 ml  $\text{CaCl}_2$   
 (C) 800 ml NaCl, 200 ml  $\text{CaCl}_2$  (D) None of these
- Q.23 Assuming complete precipitation of AgCl, calculate the sum of the molar concentration of all the ions if 2 lit of  $2\text{M Ag}_2\text{SO}_4$  is mixed with 4 lit of 1 M NaCl solution is :  
 (A) 4M (B) 2M (C) 3 M (D) 2.5 M
- Q.24 The hydrated salt  $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  undergoes 47% loss in weight on heating and becomes anhydrous. [With no other chemical product]. The value of x will be  
 (A) 3 (B) 5 (C) 7 (D) 10
- Q.25 How many litre of  $\text{C}_7\text{H}_{16}$  will be required to react with 176 gm of oxygen. If density of  $\text{C}_7\text{H}_{16}$  is 0.8 gm/L?  
 (A) 62.5 L (B) 40 L (C) 50 L (D) 80 L
- Q.26 Air contains 20% oxygen by volume, calculate the theoretical volume of air which will be required for burning  $200\text{ m}^3$  of acetylene gas completely. All volumes are measured under the same conditions of temperature and pressure.  
 (A)  $2500\text{ m}^3$  (B)  $500\text{ m}^3$  (C)  $2000\text{ m}^3$  (D)  $3000\text{ m}^3$
- Q.27 10 ml of a compound containing 'N' and 'O' is mixed with 30 ml of  $\text{H}_2$  to produce  $\text{H}_2\text{O} (l)$  and 10 ml of  $\text{N}_2 (g)$ . Molecular formula of compound if both reactants reacts completely, is  
 (A)  $\text{N}_2\text{O}$  (B)  $\text{NO}_2$  (C)  $\text{N}_2\text{O}_3$  (D)  $\text{N}_2\text{O}_5$
- Q.28 200 ml of a gaseous mixture containing CO,  $\text{CO}_2$  and  $\text{N}_2$  on complete combustion in just sufficient amount of  $\text{O}_2$  showed contraction of 40 ml. When the resulting gases were passed through KOH solution it reduces by 50 % then calculate the volume ratio of  $V_{\text{CO}_2} : V_{\text{CO}} : V_{\text{N}_2}$  in original mixture.  
 (A) 4 : 1 : 5 (B) 2 : 3 : 5 (C) 1 : 4 : 5 (D) 1 : 3 : 5
- Q.29 When 20 ml of mixture of  $\text{O}_2$  and  $\text{O}_3$  is heated, the volume becomes 29 ml and disappears in alkaline pyragallol solution. What is the volume percent of  $\text{O}_2$  in the original mixture?  
 (A) 90% (B) 10% (C) 18% (D) 2%
- Q.30 A mixture of  $\text{C}_2\text{H}_2$  and  $\text{C}_3\text{H}_8$  occupied a certain volume at 80 mm Hg. The mixture was completely burnt to  $\text{CO}_2$  and  $\text{H}_2\text{O} (l)$ . When the pressure of  $\text{CO}_2$  was found to be 230 mm Hg at the same temperature and volume, the fraction of  $\text{C}_2\text{H}_2$  in mixture is  
 (A) 0.125 (B) 0.5 (C) 0.85 (D) 0.25
- Q.31 20 mL of a mixture of CO and  $\text{H}_2$  were mixed with excess of  $\text{O}_2$  and exploded & cooled. There was a volume contraction of 23 mL. All volume measurements corresponds to room temperature ( $27^\circ\text{C}$ ) and one atmospheric pressure. Determine the volume ratio  $V_1 : V_2$  of CO and  $\text{H}_2$  in the original mixture  
 (A) 6.5 : 13.5 (B) 5 : 15 (C) 9 : 11 (D) 7 : 13



**Assertion Reason:**

Q.32 **Statement -1** : Molality of pure ethanol is lesser than pure water.

**Statement -2** : As density of ethanol is lesser than density of water.

[Given :  $d_{\text{ethanol}} = 0.789 \text{ gm/ml}$ ;  $d_{\text{water}} = 1 \text{ gm/ml}$ ]

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is false, statement-2 is true.

(D) Statement-1 is true, statement-2 is false.

Q.33 **Statement -1** : Mass of a solution of 1 litre of  $2\text{M H}_2\text{SO}_4$  [ $d_{\text{solution}} = 1.5 \text{ gm/ml}$ ] is greater than the mass of solution containing 400 gm MgO which is labelled as 40% (w/w) MgO.

**Statement -2** : Mass of  $\text{H}_2\text{SO}_4$  in 1 litre  $2\text{M H}_2\text{SO}_4$  [ $d_{\text{solution}} = 1.5 \text{ gm/ml}$ ] is greater than the mass of MgO in 1 litre 40% (w/w) MgO [ $d_{\text{solution}} = 2 \text{ gm/ml}$ ] solution.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is false, statement-2 is true.

(D) Statement-1 is true, statement-2 is false.

**More than one correct:**

Q.34 For the reaction :  $\text{MnO}_2 + 4\text{HCl} \xrightarrow{100\%} \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ , 8.7 gm  $\text{MnO}_2$  is dissolved in 500 ml of HCl solution containing 7.3 gm HCl per litre. (Mn = 55)

(A) HCl is the limiting reagent.

(B)  $\text{MnO}_2$  is the limiting reagent.

(C) 0.025 moles of  $\text{MnCl}_2$  will form.

(D) 560 ml  $\text{Cl}_2$  gas will liberate at  $0^\circ\text{C}$  and 1 atm.

Q.35 Solution(s) containing 40 gm NaOH is/are

(A) 50 gm of 80% (w/w) NaOH

(B) 50 gm of 80% (w/v) NaOH [ $d_{\text{soln.}} = 1.2 \text{ gm/ml}$ ]

(C) 50 gm of 20 M NaOH [ $d_{\text{soln.}} = 1 \text{ gm/ml}$ ]

(D) 50 gm of 5m NaOH

Q.36 The **incorrect** statement(s) regarding  $2\text{M MgCl}_2$  aqueous solution is/are ( $d_{\text{solution}} = 1.09 \text{ gm/ml}$ )

(A) Molality of  $\text{Cl}^-$  is 4.44 m

(B) Mole fraction of  $\text{MgCl}_2$  is exactly 0.035

(C) The conc. of  $\text{MgCl}_2$  is 19% w/v

(D) The conc. of  $\text{MgCl}_2$  is  $19 \times 10^4 \text{ ppm}$

**ANSWER KEY****EXERCISE-1**

- Q.1 (a) 34.2 g (b) 0.75 (c)  $N_{\text{HCOOH}} = 10^{-6} \times N_A$  (d)  $N_{\text{N atoms}} = 0.4 N_A$   
 (e)  $1.8 \times 10^{-2} \times N_A$  (f) 2 (g)  $w_{\text{CdS}} = 0.289 \text{ g}$  (h) 500 g  
 (i)  $\approx 0.9 \text{ g}$  (j) 7.22 g (k)  $n_{\text{SO}_4^{2-}} = 0.15 N_A$  (l)  $n_{\text{Ca}^{+2}} = 0.06 N_A$

Q.2 (a)  $0.1 N_A = 6.022 \times 10^{22}$

(b)  $0.12 N_A$

Q.3 70 ml

Q.4 2 : 5

Q.5  $1.2 \times 10^{23}$

Q.6 20.8 g

Q.7 0.12

Q..8 1435.3 g

Q.9 (a) 0.5

(b) 1

(c) 29.556

(d) 2

Q.10

**P****V****n****Temperature**

(i)  $16.628 \times 10^3 \text{ Pa}$

15 L

**0.1**

27°C

(ii) **0.1642 atm**

42 L

0.42 mol

200K

(iii) 304 torr

**4.926 L**

$4 \times 10^{-2}$

327°C

(iv) 380 mmHg

**24.63 L**

0.5 mol

300K

Q.11 2.34 g/L

Q.12  $P_{\text{total}} = 0.3284 \text{ atm}$

Q.13 (a) 32 g (b) 8 g (c) 4 (d) 44.8 g/mol

Q.14 120

Q.15  $M + \frac{1}{3}$

Q.16 38.15 amu

Q.17 fractional abundances = 0.6, 0.4

Q.18  $\frac{600}{13}$

Q.19 (a)  $\text{C}_2\text{H}_6\text{O}$  (b)  $\text{Fe}_2\text{O}_3$  (c)  $\text{CH}_2\text{O}$

Q.20 (a)  $\text{C}_6\text{H}_{12}$  (b)  $\text{NH}_2\text{Cl}$

Q.21 (a) Empirical formula :  $\text{CH}_2\text{O}$ ; (b) Molecular formula :  $\text{C}_2\text{H}_4\text{O}_2$

Q.22 12

Q.23  $0.16 N_A$

Q.24 30.7

Q.25 (a) 0.5 M, (b) 0.5 M, (c) 0.2 M

Q.26 1.5 m

Q.27 16.67%

Q.28 1.288 gm/ml

Q.29 (a) 4.14 (b) 20 % (c) 30% (d)  $0.0697 \approx 0.07$

Q.30 (a) 2.37 (b) 2.08 (c) 9.83

Q.31 (a) 0.15 (b) 0.016 mol (c) 0.06 (d) 0.4 (e) 0.5

Q.32  $2.7 \times 10^{-4} \text{ m}$

Q.33 0.15 M

Q.34 0.06 M

Q.35 0.8

Q.36 1.25 gm/ml

Q.37 45.45%

Q.38  $3.0 \times 10^{-3} \text{ M}$

Q.39 0.67 m, 0.67 m

| Q.40 | <b>Aqueous solution</b> | <b>Density(g/ml)</b> | <b>Mass% of solute</b> | <b>m</b> | <b>M</b> | <b>Mole fraction of solute(X)</b> |
|------|-------------------------|----------------------|------------------------|----------|----------|-----------------------------------|
|      | Urea                    | 1.2                  | 20                     | 4.17     | 4        | 0.069                             |
|      | Acetic acid             | 1.2                  | 40                     | 11.11    | 8        | 0.167                             |
|      | HCl                     | 1.5                  | 30                     | 11.74    | 12.32    | 0.174                             |
|      | Ammonia                 | 1.25                 | 20                     | 14.70    | 14.70    | 0.21                              |

- Q.41 (i) 35.71%, (ii) 0.166 (iii) 6.25 M (iv) 11.11 m
- Q.42 (i) 0.66 M, (ii) 1M (iii) 5M (iv) 3.33M (v) 2.2M
- Q.43 (a) 2.22 M (b) 2M
- Q.44 51.723 litre
- Q.45 116.8 gm
- Q.46  $264 \times 10^{10}$
- Q.47 27.6 gm
- Q.48 90 L
- Q.49 (a) both will get completely consumed, 50 molecules of  $\text{H}_2\text{O}$   
 (b)  $\text{O}_2$ , 80 molecules of  $\text{H}_2\text{O}$ .  
 (c)  $\text{H}_2$ , 100 molecules of  $\text{H}_2\text{O}$ .  
 (d)  $\text{H}_2$ , 0.5 moles of  $\text{H}_2\text{O}$ .  
 (e)  $\text{H}_2$ , 0.8 moles of  $\text{H}_2\text{O}$ .  
 (f)  $\text{O}_2$ , 8 g of  $\text{H}_2\text{O}$ .  
 (g)  $\text{H}_2$ , 45 g of  $\text{H}_2\text{O}$ .
- Q.50 (a) 2.4L (b) 6 atm (c) 9.2 atm
- Q.51
- |     |                                   |       |                        |               |                        |   |                                   |
|-----|-----------------------------------|-------|------------------------|---------------|------------------------|---|-----------------------------------|
|     | $\text{Fe}_2\text{O}_3(\text{s})$ | +     | $2\text{Al}(\text{s})$ | $\rightarrow$ | $2\text{Fe}(\text{s})$ | + | $\text{Al}_2\text{O}_3(\text{s})$ |
| (a) | $t = t_f$                         | 1 mol | 0                      |               | 2 mol                  |   | 1 mol                             |
| (b) | $t = t_f$                         | 3 mol | 0                      |               | 4 mol                  |   | 2 mol                             |
| (c) | $t = t_f$                         | 5 mol | 0                      |               | 10 mol                 |   | 5 mol                             |
| (d) | $t = t_f$                         | 0     | 0.5mol                 |               | 0.5 mol                |   | 0.25 mol                          |
- Q.52  $w_{\text{KCl require}} = 372.5 \text{ gm}$  ;  $w_{\text{Cl}_2 \text{ produce}} = 177.5 \text{ gm}$
- Q.53 Mass of  $n_{\text{HCN}} = 3825 \text{ g}$ ; Mass of  $n_{\text{H}_2\text{O}} = 7650 \text{ g}$
- Q.54  $w_{\text{CCl}_4} = 154 \text{ gm}$  ;  $w_c = 24 \text{ gm}$
- Q.55 (a) 1400 g, (b) 25%
- Q.56 142.5 gm
- Q.57 (a) 68 g (b) 25%
- Q.58 11.4
- Q.59 39.18%
- Q.60 65 %
- Q.61 61.5 gm
- Q.62 1
- Q.63 (a)  $(M_{\text{C}_{14}\text{H}_9\text{Cl}_5} \times 3) = 354.5 \times 3 = 1063.5 \text{ g}$  (b) Chloral is LR, Chlorobenzene is in excess.  
 (c)  $(4 \times 112.5) = 450 \text{ g}$  (d) 33.33%
- Q.64 Al = 66.6%
- Q.65  $\text{CaCO}_3 = 28.4\%$ ;  $\text{MgCO}_3 = 71.6\%$
- Q.66  $\text{NaHCO}_3 = 16.8 \%$ ;  $\text{Na}_2\text{CO}_3 = 83.2 \%$
- Q.67  $\approx 5.8 \text{ g}$
- Q.68 3.52 g
- Q.69 60%
- Q.70  $\text{NaHCO}_3 = 63 \%$  ,  $\text{NaCl} = 37\%$
- Q.71  $w_{\text{SiO}_2} = 0.48 \text{ g}$
- Q.72 2
- Q.73 129 gm
- Q.74 48 %, 20 %
- Q.75 9.3 %
- Q.76 56%
- Q.77 4%
- Q.78 10 %
- Q.79 1.879
- Q.80 640.0 gm
- Q.81 490 gm
- Q.82 44.8 V
- Q.83 1.7
- Q.84 5ml, 2ml, 3ml
- Q.85 10 ml
- Q.86  $\text{NO} = 44 \text{ ml}$ ;  $\text{N}_2\text{O} = 16 \text{ ml}$
- Q.87  $\text{O}_3$
- Q.88  $\text{NH}_3$
- Q.89  $\text{C}_2\text{H}_2 = 6 \text{ ml}$ ,  $\text{CO} = 14 \text{ ml}$
- Q.90 30 ml

**EXERCISE-2**

|      |    |      |   |      |   |      |     |      |    |
|------|----|------|---|------|---|------|-----|------|----|
| Q.1  | A  | Q.2  | A | Q.3  | C | Q.4  | C   | Q.5  | B  |
| Q.6  | B  | Q.7  | B | Q.8  | B | Q.9  | B   | Q.10 | C  |
| Q.11 | B  | Q.12 | C | Q.13 | D | Q.14 | B   | Q.15 | C  |
| Q.16 | B  | Q.17 | C | Q.18 | D | Q.19 | A   | Q.20 | C  |
| Q.21 | D  | Q.22 | D | Q.23 | B | Q.24 | C   | Q.25 | A  |
| Q.26 | A  | Q.27 | C | Q.28 | C | Q.29 | B   | Q.30 | A  |
| Q.31 | D  | Q.32 | B | Q.33 | D | Q.34 | ACD | Q.35 | AC |
| Q.36 | BD |      |   |      |   |      |     |      |    |

**EXERCISE-1 (Subjective Questions)****INTERCONVERSIONS OF CONCENTRATION TERMS**

- Q.1 Calculate the mole ratio of  $C_2H_5OH$  and  $CH_3OH$  in aqueous solution if molality of  $C_2H_5OH$  is 40/9 and mole fraction of  $CH_3OH$  is 0.1 in solution.
- Q.2 Molarity of aqueous NaOH solution will be, if mole fraction of NaOH in the solution is 0.5.  
[Given : Density of pure NaOH = 4 gm/ml]
- Q.3 The density of toluene ( $C_7H_8$ ) is 0.8 g/ml and density of thiophene ( $C_4H_4S$ ) is 1 g/ml. A solution is made by dissolving 8.4 g of thiophene in 250 ml of toluene calculate  
(a) mole fraction of thiophene in the solution.  
(b) molality of thiophene in the solution  
(c) Assuming that volume of solute and solvent are additive, what is the molarity of thiophene in the solution.
- Q.4 Commercial aqueous nitric acid has density 1.4 g/ml and molarity 15 M. Calculate the percentage of  $HNO_3$  by mass in the solution.
- Q.5 Calculate molality of 2M aqueous solution of NaOH having density 1.2 g/ml.

**RAOULT'S LAW & DALTON'S LAW IN BINARY LIQUID SOLUTION**

- Q.6 The vapour pressure of ethanol and methanol are 44.5 mm Hg and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.
- Q.7 Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50. The vapour pressure of pure benzene is 119 torr; that of toluene is 37 torr at the same temperature.
- Q.8 What is the composition of the vapour which is in equilibrium at  $30^\circ C$  with a benzene-toluene solution with a mole fraction of benzene of 0.40? With a mole fraction of benzene of 0.60?  
 $P_b^\circ = 119 \text{ torr}$  and  $P_t^\circ = 37 \text{ torr}$
- Q.9 At  $90^\circ C$ , the vapour pressure of toluene is 400 torr and that of s-xylene is 150 torr. What is the composition of the liquid mixture that boils at  $90^\circ C$ , when the pressure is 0.50 atm? What is the composition of vapour produced?
- Q.10 Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?
- Q.11 Benzene and toluene form two ideal solution A and B at 313 K. Solution A (total pressure  $P_A$ ) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure  $P_B$ ). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of  $P_A/P_B$ .

**RAOULT'S LAW & VAPOUR PRESSURE LOWERING**

- Q.12 Calculate the mass of propylene glycol( $C_3H_8O_2$ ) that must be added to 0.54 Kg of water to reduce its vapour pressure by 3 torr at  $40^\circ C$ .  
[Given : Vapour pressure of water at  $40^\circ C$  is 25 torr]
- Q.13 At  $25^\circ C$ , the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of  $CH_3OH$  in a solution in which the (partial) vapor pressure of  $CH_3OH$  is 23.0 torr at  $25^\circ C$ ?
- Q.14 The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?
- Q.15 The vapour pressure of pure water at  $26^\circ C$  is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 g glucose,  $C_6H_{12}O_6$ , in 70 g water?
- Q.16 The vapour pressure of pure water at  $25^\circ C$  is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.
- Q.17 Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt.100) are dissolved in 432 g water.
- Q.18 What weight of the non-volatile solute, urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?
- Q.19 The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.
- Q.20 The vapour pressure of pure benzene at  $25^\circ C$  is 639.7 mm of Hg and the vapour pressure of a solution of a solute in  $C_6H_6$  at the same temperature is 631.7 mm of Hg. Calculate molality of solution.
- Q.21 The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?
- Q.22 The vapour pressure of water is 17.54 mm Hg at 293K. Calculate vapour pressure of 0.5 molal solution of a solute in it.

**BOILING POINT ELEVATION AND FREEZING POINT DEPRESSION**

- Q.23 When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised  $0.284^\circ C$ . What is the molecular weight of the substance? Molal boiling point constant for ether is  $2.11^\circ C \cdot kg/mol$ .
- Q.24 A solution containing 3.24 g of a nonvolatile nonelectrolyte and 200 g of water boils at  $100.130^\circ C$  at 1 atm. What is the molecular weight of the solute? ( $K_b$  for water  $0.513^\circ C/m$ )
- Q.25 The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at  $99.725^\circ C$ . ( $K_b$  for water  $0.513^\circ C/m$ )
- Q.26 An aqueous solution of a nonvolatile solute boils at  $100.17^\circ C$ . At what temperature will this solution freeze? [ $K_f$  for water  $0.52^\circ C/m$ ]

- Q.27 Pure benzene freeze at  $5.45^{\circ}\text{C}$ . A solution containing 7.24 g of  $\text{C}_2\text{H}_2\text{Cl}_4$  in 115.3 g of benzene was observed to freeze at  $3.55^{\circ}\text{C}$ . What is the molal freezing point constant of benzene?
- Q.28 A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at  $-0.465^{\circ}\text{C}$ . Determine the molecular weight of the solute. [ $K_f$  for water  $1.86^{\circ}\text{C/m}$ ]
- Q.29 The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is  $0.10^{\circ}\text{C}$  lower than that of pure benzene. What is the molecular weight of the compound? ( $K_f$  is  $5.12^{\circ}\text{C/m}$  for benzene)
- Q.30 The elements X and Y form compounds having molecular formula  $\text{XY}_2$  and  $\text{XY}_4$ . When dissolved in 20 gm of benzene, 1 gm  $\text{XY}_2$  lowers the freezing point by  $2.3^{\circ}$ , whereas 1 gm of  $\text{XY}_4$  lowers the freezing point by  $1.3^{\circ}\text{C}$ . The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.
- Q.31 Calculate the molal elevation constant,  $K_b$  for water and the boiling point of 0.1 molal urea solution. Latent heat of vaporisation of water is  $9.72 \text{ kcal mol}^{-1}$  at  $373.15 \text{ K}$ .
- Q.32 A solution of 0.643 g of an organic compound in 50ml of benzene (density ; 0.879 g/ml) lowers its freezing point from  $5.51^{\circ}\text{C}$  to  $5.03^{\circ}\text{C}$ . If  $K_f$  for benzene is 5.12 K, calculate the molecular weight of the compound.
- Q.33 What is the freezing point of an aqueous solution that boils at  $104^{\circ}\text{C}$  ?  
[Given :  $K_f = 1.86^{\circ}\text{C/m}$ ,  $K_b = 0.51^{\circ}\text{C/m}$ ]
- Q.34 How many gram of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) must be added to 0.4 Kg of water to produce a solution that freezes at  $-5^{\circ}\text{C}$  ?
- Q.35 Calculate freezing and boiling points of each of following solutions :  
(a) 0.25 m glucose in ethanol.  
(b) 20 g of decane in 50g  $\text{CHCl}_3$ .  
(c) 4 g NaOH in 200g of water.  
(d) 0.45 mol ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) & 0.15 mol KBr in 200g  $\text{H}_2\text{O}$ .

**Given :**

| S.No. | Solvent                                     | Normal Boiling Point( $^{\circ}\text{C}$ ) | $K_b$ ( $^{\circ}\text{C/m}$ ) | Normal freezing Point( $^{\circ}\text{C}$ ) | $K_f$ ( $^{\circ}\text{C/m}$ ) |
|-------|---------------------------------------------|--------------------------------------------|--------------------------------|---------------------------------------------|--------------------------------|
| 1.    | Water ( $\text{H}_2\text{O}$ )              | 100                                        | 0.51                           | 0                                           | 1.86                           |
| 2.    | Chloroform ( $\text{CHCl}_3$ )              | 61.2                                       | 3.63                           | - 63.5                                      | 4.68                           |
| 3.    | Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) | 78.4                                       | 1.22                           | - 114.6                                     | 2                              |

- Q.36 The cryoscopic constant for acetic acid is  $3.6 \text{ K kg/mol}$ . A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at  $16.14^{\circ}\text{C}$  instead of the usual  $16.60^{\circ}\text{C}$ . The hydrocarbon contains 92.3% carbon. What is the molecular formula?

- Q.37 Match the boiling point with  $K_b$  for x, y and z, if molecular weight of x, y and z are same.

|   | b.pt. | $K_b$ |
|---|-------|-------|
| x | 100   | 0.68  |
| y | 27    | 0.53  |
| z | 253   | 0.98  |



**OSMOTIC PRESSURE**

- Q.38 Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm.  $K_f(\text{water}) = 1.86 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}$ .
- Q.39 At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.
- Q.40 At 10°C, the osmotic pressure of urea solution is 500 mm of Hg. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm of Hg. Determine extent of dilution.
- Q.41 The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per L for an intravenous injection that is to have the same osmotic pressure as blood?
- Q.42 What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) per 150 cm<sup>3</sup> of solution?
- Q.43 A 250 mL water solution containing 48.0 g of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?
- Q.44 A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm<sup>3</sup> of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm<sup>3</sup>. Determine the molecular weight of the protein.
- Q.45 The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100 cm<sup>3</sup> of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cm<sup>3</sup>. What is the molecular weight of the polyisobutylene?
- Q.46 A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877% (w/v) of urea solution. Find molecular weight of urea.
- Q.47 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 gm of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

**VAN'T HOFF FACTOR & COLLIGATIVE PROPERTIES**

- Q.48 A storage battery contains a solution of  $\text{H}_2\text{SO}_4$  38% by weight. What will be the Van't Hoff factor if the  $\text{DT}_{f(\text{experiment})}$  is 29.08. [Given  $K_f = 1.86 \text{ mol}^{-1} \text{ Kg}$ ]
- Q.49 A certain mass of a substance, when dissolved in 100 g  $\text{C}_6\text{H}_6$ , lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100g water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water?  $K_f$  for  $\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_6$  are 1.86 and 5.12K kg mol<sup>-1</sup>.



- Q.50 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant ( $K_f$ ) of benzene is  $4.9 \text{ K.kg.mol}^{-1}$ . What is the percentage association of the acid?
- Q.51 A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. ( $R=8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )
- Q.52 The freezing point of a solution containing 0.2 g of acetic acid in 20.0g of benzene is lowered by  $0.45^\circ\text{C}$ . Calculate the degree of association of acetic acid in benzene. ( $K_f$  for benzene =  $5.12 \text{ K mol}^{-1} \text{ kg}$ )
- Q.53 0.85 % (w/v) aqueous solution of  $\text{NaNO}_3$  is apparently 90% dissociated at  $27^\circ\text{C}$ . Calculate its osmotic pressure. ( $R= 0.082 \text{ l atm K}^{-1} \text{ mol}^{-1}$ )
- Q.54 A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.
- Q.55 To  $500 \text{ cm}^3$  of water,  $3 \times 10^{-3} \text{ kg}$  of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point?  $K_f$  and density of water are  $1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$  and  $0.997 \text{ g cm}^{-3}$  respectively.
- Q.56 The Henry law constant for  $\text{O}_2(\text{g})$  and  $\text{N}_2(\text{g})$  in water at  $0^\circ\text{C}$  are  $2.5 \times 10^4 \text{ bar}$  and  $5.0 \times 10^4 \text{ bar}$  respectively. Calculate  $DT_f$  of solution made by dissolving air at 1 bar pressure.  
[Given : mole % of  $\text{O}_2$  in air = 20 & mole % of  $\text{N}_2$  in air = 80]  
 $K_f$  of  $\text{H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$   
**[Write your answer by multiplying with  $10^5$ ]**
- Q.57 List the following solution :  
(a) 0.12 M glucose      (b) 0.05 M LiBr      (c) 0.05 M  $\text{Ca}(\text{NO}_3)_2$       (d) 0.05  $\text{AlCl}_3$   
(i) In order of increasing boiling point  
(ii) In order of increasing freezing point  
(iii) In order of increasing vapour pressure
- Q.58 The osmotic pressure of a 0.01 M aqueous solution of  $\text{CaCl}_2$  is found to be 0.4926 atm at  $27^\circ\text{C}$ .  
(a) Calculate the vant' Hoff factor(i) for the solution.  
(b) How would you expect the value of (i) to change as solution becomes more concentrated.

**HENRY'S LAW**

- Q.59 Calculate concentration of  $\text{CO}_2(\text{mol/L})$  in a soft drink that is bottled with a partial pressure of  $\text{CO}_2$  of 5atm over the liquid at  $25^\circ\text{C}$ . The Henry's Law constant for  $\text{CO}_2$  in water at this temperature is  $16.33 \times 10^2 \text{ atm}$ .
- Q.60 At a particular temperature and at a pressure of 1 atm, mass & volume of  $\text{O}_3$  that can be dissolved in 1L of  $\text{H}_2\text{O}$  is m gram and Vml respectively (Assuming ideal gas behaviour of  $\text{O}_3$  and assuming  $\text{O}_3$  does not associate or dissociate in solution). Calculate the mass and volume of  $\text{O}_3$  dissolved in 2L of  $\text{H}_2\text{O}$  at same T and at a pressure of 5 atm.
- Q.61 Henry's law constant for  $\text{CO}_2$  in water is  $1.67 \times 10^8 \text{ Pa}$  at 298 K. Calculate the quantity of  $\text{CO}_2$  in 500 mL of soda water when packed under 2.5 atm  $\text{CO}_2$  pressure at 298 K.

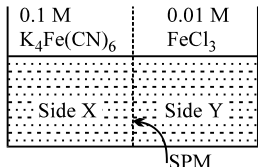
## EXERCISE-2 (Objective Questions)

Single correct :

- Q.1 Mole fraction of A vapours above the solution in mixture of A and B ( $X_A = 0.4$ ) will be  
[Given :  $P_A^\circ = 100$  mm Hg and  $P_B^\circ = 200$  mm Hg]  
(A) 0.4 (B) 0.8 (C) 0.25 (D) none of these
- Q.2 Identify the **incorrect** statement :  
(A) Solubility of gas increases on decreasing temperature.  
(B) Henry's constant increases on increasing temperature.  
(C) Pressure has negligible effect on solubility of solid.  
(D) Solubility of solid will always increase on increasing temperature.
- Q.3 The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are  
(A) 0.15 (B) 5.7 (C) 0.2 (D) 4.0
- Q.4 At a given temperature, total vapour pressure (**in torr**) of a mixture of volatile components A and B is given by  
$$P_{\text{Total}} = 120 - 75 X_B$$
  
hence, vapour pressure of pure A and B respectively (**in torr**) are  
(A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45
- Q.5 Which of the following plots represents an ideal binary mixture?  
(A) Plot of  $P_{\text{total}}$  v/s  $1/X_B$  is linear ( $X_B$  = mole fraction of 'B' in liquid phase).  
(B) Plot of  $P_{\text{total}}$  v/s  $Y_A$  is linear ( $Y_B$  = mole fraction of 'A' in vapour phase)  
(C) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_A$  is linear (D) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_B$  is non linear
- Q.6 Two liquids A & B form an ideal solution. What is the vapour pressure of solution containing 2 moles of A and 3 moles of B at 300 K? [Given : At 300 K, Vapour pr. of pure liquid A ( $P_A^\circ$ ) = 100 torr, Vapour pr. of pure liquid B ( $P_B^\circ$ ) = 300 torr]  
(A) 200 torr (B) 140 torr (C) 180 torr (D) None of these
- Q.7 At 300 K, the vapour pressure of an ideal solution containing 3 mole of A and 2 mole of B is 600 torr. At the same temperature, if 1.5 mole of A & 0.5 mole of C (non-volatile) are added to this solution the vapour pressure of solution increases by 30 torr. What is the value of  $P_B^\circ$ ?  
(A) 940 (B) 405 (C) 90 (D) none of these
- Q.8 Two liquid A and B form an ideal solution. The ratio of vapour pressures of pure liquids A and B are 3 : 5. if the mole- fraction of A in the liquid solution at equilibrium with vapours, is 0.4, then the mole- fraction of B in the vapour is  
(A)  $\frac{3}{5}$  (B)  $\frac{5}{7}$  (C)  $\frac{2}{7}$  (D)  $\frac{2}{5}$
- Q.9 Which of the following solutions can have boiling point less than that of both the individual components?  
(A) n-Hexane & n-Heptane (B)  $\text{CHCl}_3$  &  $\text{CH}_3\text{COCH}_3$   
(C)  $\text{HNO}_3$  &  $\text{H}_2\text{O}$  (D)  $\text{C}_2\text{H}_5\text{OH}$  &  $\text{H}_2\text{O}$

- Q.10 With increase of temperature, which of these changes  
 (A) Molality (B) Weight fraction of solute  
 (C) Volume fraction of solute present in water (D) Mole fraction
- Q.11 In mixture A and B components show -ve deviation as  
 (A)  $\Delta V_{\text{mix}} > 0$   
 (B)  $\Delta H_{\text{mix}} < 0$   
 (C) A-B interaction is weaker than A-A and B-B interaction  
 (D) A-B interaction is same as that of A-A and B-B interaction
- Q.12 Pressure cooker reduces cooking time for food because  
 (A) Heat is more evenly distributed in the cooking space  
 (B) Boiling point of water involved in cooking is increased  
 (C) The higher pressure inside the cooker crushes the food material  
 (D) Cooking involves chemical changes helped by a rise in temperature
- Q.13 The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg  
 (A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8
- Q.14 The vapour pressure of pure benzene at a certain temperature is 0.950 bar. A non-volatile, non-electrolyte solid weighing 0.5 gm is added to 39.0 gm of benzene, vapour pressure of the solution becomes 0.945 bar. What is the molar mass of the solid substance?  
 (A)  $160 \text{ gm mol}^{-1}$  (B)  $210 \text{ gm mol}^{-1}$  (C)  $95 \text{ gm mol}^{-1}$  (D)  $189 \text{ gm mol}^{-1}$
- Q.15 Which of the following option represent **correct** order of vapour pressure of given aqueous solutions:  
 (A)  $0.01 \text{ m Al}_2(\text{SO}_4)_3 > 0.01 \text{ m BaCl}_2 > 0.01 \text{ m NaCl} > 0.01 \text{ m glucose}$   
 (B)  $0.01 \text{ m BaCl}_2 > 0.01 \text{ m NaCl} > 0.01 \text{ m CH}_3\text{COOH}$   
 (C)  $0.01 \text{ m glucose} > 0.01 \text{ m CH}_3\text{COOH} > 0.01 \text{ m KCl}$   
 (D)  $0.01 \text{ m BaCl}_2 = 0.01 \text{ m KCl} = 0.01 \text{ m glucose}$
- Q.16 The correct relationship between the boiling points of very dilute solution of  $\text{AlCl}_3$  ( $T_1\text{K}$ ) and  $\text{CaCl}_2$  ( $T_2\text{K}$ ) having the same molar concentration is  
 (A)  $T_1 = T_2$  (B)  $T_1 > T_2$  (C)  $T_2 > T_1$  (D)  $T_2 \neq T_1$
- Q.17 What will be the molecular weight of  $\text{CaCl}_2$  determined in its aq. solution experimentally from depression of freezing point?  
 (A) 111 (B)  $< 111$  (C)  $> 111$  (D) data insufficient
- Q.18 1.0 molal aqueous solution of an electrolyte  $\text{A}_2\text{B}_3$  is 60% ionised. The boiling point of the solution at 1 atm is ( $K_{\text{b(H}_2\text{O)}} = 0.52 \text{ K kg mol}^{-1}$ )  
 (A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K
- Q.19 The vapour pressure of an aqueous solution is found to be 750 torr at certain temperature 'T'. If 'T' is the temperature at which pure water boils under atmospheric pressure and same solution show elevation in boiling point  $\Delta T_{\text{b}} = 1.04 \text{ K}$ , find the atmospheric pressure ( $K_{\text{b}} = 0.52 \text{ K kg mol}^{-1}$ )  
 (A) 777 (B) 779 (C) 782 (D) 746

- Q.20 Which of the following ideal aqueous solutions will show maximum boiling point?  
 (A) 0.5 M NaCl showing 50% dissociations  
 (B) 0.3 M  $K_2Fe[Fe(CN)_6]$   
 (C) 1 M Glucose solution  
 (D) 1 mole of AgCl is mixed with 0.5 l of  $H_2O$
- Q.21 Which of the following solution is expected to have minimum freezing point?  
 (A) 0.1 M NaCl (B) 0.1 M Glucose (C) 0.1 M  $CaCl_2$  (D) 0.08 M  $Na_2SO_4$
- Q.22 A 0.040 M solution of each of the following compound is prepared which solution would you expect to freeze at  $-0.149^\circ C$ ? [ $K_f(\text{water}) = 1.86 \text{ K Kg mol}^{-1}$ ]  
 [Assume very dilute aqueous solution]  
 (A)  $[Co(en)_2Cl_2]Cl$  (B)  $K_4[Fe(CN)_6]$   
 (C)  $[Cr(Py)_5Cl]Cl_2$  (D)  $[Cr(NH_3)_6]Cl_3$
- Q.23 Equal volume of 0.1 M KI and 0.1 M  $AgNO_3$  solutions are mixed., The depression of freezing point of the resulting dilute aqueous solution will be -  
 [Given :  $K_f(H_2O) = 1.86 \text{ K-Kg/mole}$ ]  
 (A)  $0.093^\circ C$  (B)  $9.3^\circ C$  (C)  $1.86^\circ C$  (D)  $0.186^\circ C$
- Q.24 The freezing point of 0.2 M HA acid is  $-0.558^\circ C$ . The dissociation constant of acid is  
 (Given:  $K_f = 1.86^\circ C/m$ )  
 (A) 0.05 (B) 0.5 (C) 0.01 (D) 0.1
- Q.25 How many grams of sucrose (molecular weight = 342) should be dissolved in 100 gm water in order to produce a solution with a  $105^\circ C$  difference between the freezing point and the boiling point temperature?  
 ( $K_f = 1.86 \text{ K Kg/mol}$ ,  $K_b = 0.51 \text{ K Kg/mol}$ )  
 (A) 34.2 gm (B) 72 gm (C) 342 gm (D) 460 gm
- Q.26 Liquid benzene freezes at  $7^\circ C$  and boils at  $77^\circ C$ . If the  $K_f$  and  $K_b$  values for benzene are  $5.0 \text{ K-Kg/mol}$  and  $2.50 \text{ K-Kg/mol}$  respectively, calculate the ratio of the molar latent heat of fusion to the molar latent heat of vaporisation.  
 (A) 3.125 (B) 0.4 (C) 1.28 (D) 0.32
- Q.27 0.2 molal solution each of Glucose (I), Magnesium chloride (II) and Aluminium sulphate (III) is taken. The **correct** order freezing point of the solutions will be :  
 (A) All same  
 (B)  $(\text{freezing point})_I < (\text{freezing point})_{II} < (\text{freezing point})_{III}$   
 (C)  $(\text{freezing point})_{III} < (\text{freezing point})_I < (\text{freezing point})_{II}$   
 (D)  $(\text{freezing point})_I > (\text{freezing point})_{II} > (\text{freezing point})_{III}$
- Q.28 Freezing point of an aqueous solution is  $(-0.186)^\circ C$ . Elevation of boiling point of the same solution is  $K_f = 1.86^\circ C$ .  $K_b = 0.512^\circ$  find the increase in boiling point  
 (A)  $0.186^\circ C$  (B)  $0.0512^\circ C$  (C)  $0.092^\circ C$  (D)  $0.02372^\circ C$
- Q.29 The van't Hoff factor for 0.1 M  $Ba(NO_3)_2$  solution is 2.74. The degree of dissociation is  
 (A) 91.3% (B) 87% (C) 100% (D) 74%

- Q.30 In a 0.2 molal aqueous solution of weak acid HX (the degree of dissociation 0.3) the freezing point is (Given :  $K_f = 1.85 \text{ K molality}^{-1}$ ) :  
 (A)  $-0.26^\circ\text{C}$  (B)  $+48^\circ\text{C}$  (C)  $-0.48^\circ\text{C}$  (D)  $-0.36^\circ\text{C}$
- Q.31 A  $\text{CaCl}_2$  aqueous solution at  $27^\circ\text{C}$  has an osmotic pressure 16 atm and density of 1.2 gm/ml. What is freezing point of this solution [ $K_f$  of water =  $1.8 \text{ K Kg mol}^{-1}$ ,  $R = 0.08 \text{ atm litre / mole - K}$ ]  
 (A)  $3.2^\circ\text{C}$  (B)  $-3.2^\circ\text{C}$  (C)  $1.02^\circ\text{C}$  (D)  $-1.02^\circ\text{C}$
- Q.32 Calculate amount of  $\text{CaCl}_2$  dissolved in 16.42 litre of water such that its osmotic pressure is 1 atm at  $27^\circ\text{C}$ .  
 (A) 74 gm (B) 12.33 gm (C) 24.67 gm (D) 6.16 gm
- Q.33 Two binary aqueous solutions A and B with same non volatile solute are separated by a semipermeable membrane. A has higher vapour pressure than B then :  
 (A) solvent will flow from A to B solution.  
 (B) solvent will flow from B to A solution.  
 (C) can not predict net direction of movement of solvent by given information.  
 (D) There will be no net flow of solvent
- Q.34  $\text{FeCl}_3$  on reaction with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in aqueous solution gives blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is  
 (A) blue colour formation in side X.  
 (B) blue colour formation in side Y.  
 (C) blue colour formation in both of the sides X and Y.  
 (D) no blue colour formation.
- 
- Q.35 In the depression of freezing point experiment, it is found that  
 (I) The vapour pressure of the solution is less than that of pure solvent.  
 (II) The vapour pressure of the solution is more than that of pure solvent.  
 (III) Only solute molecules solidify at the freezing point.  
 (IV) Only solvent molecules solidify at the freezing point.  
 (A) I, II (B) II, III (C) I, IV (D) I, II, III

### Assertion & Reasoning type questions

- Q.36 **Statement-1:** Except osmotic pressure, all other colligative properties depends on the nature of solvent.  
**Statement-2:** Colligative properties of any solution are intensive properties.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- Q.37 **Statement-1:** Additon of ethylene glycol (non-volatile) to water lowers the freezing point of water hence used as antifreeze.  
**Statement-2:** Addition of any substance to water lowers its freezings point.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.



**Comprehension****Paragraph for question nos. 38 & 39**

A tree is exactly 10 m tall. If sap rises to top of tree by osmotic pressure at 27°C and assume ground water outside tree is pure water and density of sap is 1 gm/ml. Then :

[Given :  $g = 10 \text{ m/s}^2$ ,  $R = 0.08 \text{ bar litre/mol K}$ ]

[sap = fluid which circulates in vascular system of plant.]

- Q.38 What must be the molarity of solute in sap?  
 (A)  $\frac{10}{24} \text{ M}$  (B)  $10^5 \text{ M}$  (C)  $\frac{1}{24} \text{ M}$  (D)  $\frac{1}{12} \text{ M}$
- Q.39 If only solute in sap is  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  then what is its % by mass.  
 (A) 1.425 % (B) 14.25 % (C) 28.5 % (D) 2.85 %

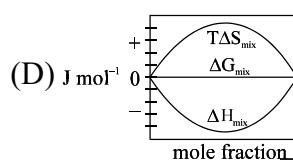
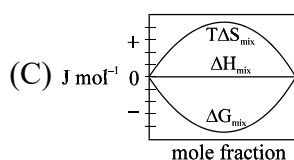
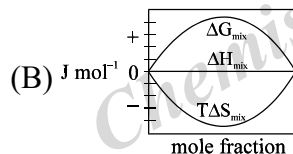
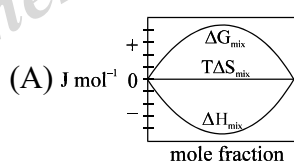
**Paragraph for question nos. 40 to 42**

Colligative properties i.e. the properties of solution which depend upon the number of particles present in solution are osmotic pressure, depression in freezing point, elevation in boiling point and lowering in vapour pressure. Experimental values of colligative properties for electrolytes are always higher than those obtained theoretically because electrolytes dissociate to furnish more ions in solution. On the other hand experimentally obtained values of colligative properties for associating nature of solute are lower than those obtained theoretically. The ratio of experimental colligative properties to theoretical colligative properties is called vant Hoff factor(i).

- Q.40 Vant Hoff factor(i) for dimerisation of acetic acid in chlorobenzene, assuming 30% degree of association is:  
 (A) 0.85 (B) 0.95 (C) 0.90 (D) 0.7
- Q.41 For 1 M solution of mono basic acid HA having  $\alpha > 0.05$ , the dissociation constant  $K_a$  in terms of vant Hoff factor(i) can be written as  
 (A)  $\frac{(i-1)}{i}$  (B)  $\frac{(i+1)}{i}$  (C)  $(i-1)^2$  (D)  $\frac{(i-1)^2}{(2-i)}$
- Q.42 The **correct** order of osmotic pressure for the solutions assuming complete dissociation of electrolytes.  
 (i) 1M urea (ii) 1M NaCl (iii) 1M  $\text{Na}_2\text{SO}_4$  (iv) 1M  $\text{Na}_3\text{PO}_4$   
 (A) (i) > (ii) > (iii) > (iv) (B) (iv) > (iii) > (ii) > (i)  
 (C) (ii) > (iii) > (iv) > (i) (D) (i) > (iv) > (iii) > (ii)

**More than one may be correct**

- Q.43 The boiling point of an aqueous urea solution is 101.04°C. The density of solution is 1.12 gm/ml. Which of the following is/are **correct** statement(s) regarding this solution?  
 [Given : For water :  $K_b = 0.52 \text{ K-Kg mol}^{-1}$ ,  $K_f = 1.86 \text{ K-Kg mol}^{-1}$ ]  
 (A) The molarity of solution is 2M.  
 (B) The freezing point of solution is 3.72°C.  
 (C) If the solution is cooled to  $-1.86^\circ\text{C}$ , no ice will form.  
 (D) At any temperature, the relative lowering of vapour pressure is  $\left(\frac{9}{259}\right)$ .
- Q.44 Which of the following represents incorrectly the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution.



- Q.45 Identify the **correct** statement(s) :
- (A) Colligative property of any solution is intensive quantity.  
 (B) Osmotic pressure is independent of nature of solvent.  
 (C) Elevation in boiling point depends on nature of solvent.  
 (D) Osmotic pressure is widely used to determine molar masses of protein, polymer and other micromolecules.
- Q.46 Acetone & chloroform form a non ideal solution. If 116 gm of acetone is mixed with 239 gm of chloroform & their vapour pressures in pure state at 298 K are 360 torr & 300 torr respectively then what can not be vapour pressure of the above solution at 298 K.  
 (A) 330 torr (B) 350 torr (C) 250 torr (D) 370 torr
- Q.47 Consider 0.1 M solution of two non volatile solutes X and Y. The solute X behave as univalent electrolyte, while the solute Y dimerises in solution. Select correct statements regarding these solutions -  
 (A) The freezing point of solution of X will be higher than that of Y.  
 (B) The osmotic pressure of solution of Y will be lower than that of X.  
 (C) The boiling point of solution of X will be higher than that of Y.  
 (D) The vapour pressure of solution of Y will be lower than that of X.
- Q.48 Which of the following solutions is/are hypertonic with 0.4 M NaCl showing 80% dissociation.  
 (A) 0.7 M Glucose  
 (B) 0.3 M  $\text{Na}_3\text{PO}_4$  showing 90% dissociation  
 (C) 1 M  $\text{CH}_3\text{COOH}$  showing 30 % association  
 (D) 0.5 M  $\text{CaCl}_2$  showing 20 % dissociation

**Match the column:**

- | Q.49 | Column I<br>(Colligative properties)                                                                                                                                        | Column II<br>(Aqueous solution)<br>(Assume $m = M$ ) |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|
| (A)  | $\Delta T_f = 0.3 \times K_f$                                                                                                                                               | (P) 0.1 m – $\text{Ca}(\text{NO}_3)_2$               |
| (B)  | $\Delta T_b = 0.28 \times K_b$                                                                                                                                              | (Q) 0.14 m – NaBr                                    |
| (C)  | $p^0 - p = 0.19 \times RT \left( \frac{\Delta T_f}{K_f} \right)$                                                                                                            | (R) 0.1 m – $\text{MgCl}_2$ ( $\alpha = 0.9$ )       |
| (D)  | $\frac{p^0 - p}{p^0} = \frac{\left( \frac{1000}{18} \right) \left( \frac{\Delta T_f}{K_f} \right)}{\left( \frac{1000}{18} \right) + \left( \frac{\Delta T_f}{K_f} \right)}$ | (S) 0.28 m – Urea                                    |
|      |                                                                                                                                                                             | (T) 0.1 m – HA (monobasic acid, $K_a = 0.81$ )       |

- | Q.50 | List - I<br>(Solution)                               | List - II<br>(Nature of solution)                                                                                                      |
|------|------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| (A)  | Phenol and Aniline                                   | (P) +ve deviation from Raoult's Law                                                                                                    |
| (B)  | Methanol and Acetone                                 | (Q) Molarity = Molality                                                                                                                |
| (C)  | 5 M NaOH solution<br>having $d = 1.25 \text{ gm/ml}$ | (R) Actual colligative properties will be different as compare to expected colligative properties even after considering dissociation. |
| (D)  | $5 \times 10^{-3} \text{ M}$ aqueous KOH solution    | (S) –ve deviation from Raoult's Law                                                                                                    |

## ANSWER KEY

## EXERCISE -1

- Q.1 0.66 Q.2 35.71 Q.3 (a) 0.044 (b) 0.5 (c) 0.386  
 Q.4 67.5% Q.5 1.785 molal Q.6 66.13 mm Hg  
 Q.7 0.237 Q.8  $y_b = 0.682, y_t = 0.318; y_b = 0.829, y_t = 0.171$   
 Q.9 92 mol% toluene; 96.8 mol % toluene Q.10  $P_A^\circ = 213.33 \text{ torr}, P_B^\circ = 960.0 \text{ torr}$   
 Q.11 0.964 Q.12 310.9 g Q.13 0.24  
 Q.14 0.25 Q.15 24.5 torr Q.16 57.24 g/mol  
 Q.17 0.04 Q.18 111.1g, 18.52 molal Q.19 0.741 m, 0.013  
 Q.20 0.162 m Q.21 65.25  
 Q.22 17.38 Q.23 106 g/mol  
 Q.24 64.0 g/mol Q.25 100.079°C  
 Q.26  $-0.62^\circ\text{C}$  Q.27  $5.08^\circ\text{C/m}$   
 Q.28 50.8 g/mol Q.29 2048 g/mol  
 Q.30  $x = 25.6, y = 42.6$  Q.31  $K_b = 0.512 \text{ kg mol K}^{-1}, T_b = 373.20 \text{ K}$   
 Q.32 156.06 Q.33  $-14.59^\circ\text{C}$   
 Q.34 66.67 g  
 Q.35 (a)  $T_b = 78.705^\circ\text{C}, T_f = -115.1^\circ\text{C};$  (b)  $T_b = 71.4^\circ\text{C}, T_f = -76.65^\circ\text{C}$   
 (c)  $T_b = 100.51^\circ\text{C}, DT_f = -1.86^\circ\text{C};$  (d)  $T_b = 101.9125^\circ\text{C}, T_f = -6.975^\circ\text{C}$   
 Q.36  $\text{C}_6\text{H}_6$  Q.37  $K_b(x) = 0.68, K_b(y) = 0.53, K_b(z) = 0.98$   
 Q.38  $T_f = -2.28^\circ\text{C}$  Q.39  $P = 0.2217 \text{ atm}$  should be applied  
 Q.40  $(V_{\text{final}} = 5 \cdot V_{\text{original}})$  Q.41 54 g  
 Q.42 0.81 atm Q.43 13.8 atm  
 Q.44  $5.4 \times 10^5 \text{ g/mol}$  Q.45  $2.4 \times 10^5 \text{ g/mol}$   
 Q.46 59.99 Q.47  $M_A/M_B = 0.33$   
 Q.48  $i = 2.5$  Q.49 3 ions  
 Q.50  $a = 99.2\%$  Q.51  $7.482 \times 10^5 \text{ Nm}^{-2}$   
 Q.52 94.5 % Q.53 4.67 atm  
 Q.54 0.95; 1.95 Q.55 0.229  
 Q.56 248  
 Q.57 (i)  $b < a < c < d;$  (ii)  $d < c < a < b;$  (iii)  $d < c < a < b$   
 Q.58 (a) 2 (b) 'i' will increase. Q.59 0.167M  
 Q.60 10M gram, 2V ml Q.61 1.854 gm

## EXERCISE -2

- Q.1 C Q.2 D Q.3 B Q.4 C Q.5 C  
 Q.6 D Q.7 C Q.8 B Q.9 D Q.10 C  
 Q.11 B Q.12 B Q.13 C Q.14 D Q.15 C  
 Q.16 B Q.17 B Q.18 D Q.19 A Q.20 B  
 Q.21 C Q.22 A Q.23 D Q.24 D Q.25 B  
 Q.26 D Q.27 D Q.28 B Q.29 B Q.30 C  
 Q.31 D Q.32 C Q.33 A Q.34 D Q.35 C  
 Q.36 D Q.37 C Q.38 C Q.39 A Q.40 A  
 Q.41 D Q.42 B Q.43 ACD Q.44 ABD Q.45 ABCD  
 Q.46 ABD Q.47 BC Q.48 BC  
 Q.49 (A) P (B) Q,R,S (C) T (D) P,Q,R,S,T  
 Q.50 (A) S (B) P (C) R (D) Q



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